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# AMERICAN JOURNAL OF SCIENCE

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American Journal of Science

*SEPTEMBER 1956*

# ZIRCON IN ROCKS. 2. IGNEOUS ROCKS

ARIE POLDERVAART

ABSTRACT. This paper attempts to summarize observations on zircon concentrates of igneous rocks from the literature and the writer's work on southern African and American rocks. The crystallization of zircon is late in the consolidation of basaltic magma, early in that of dioritic or granitic magma, but increasingly delayed in alkaline magmas, apparently in keeping with the rank of the rocks in the alkaline series. In magmatic plutons in which zircon crystallized early, the characters and size of the zircons remain the same throughout. Zircon measurements can thus be used to fingerprint igneous rocks.

## INTRODUCTION

A survey of the literature shows that a number of claims of great significance to petrogenesis have been made concerning zircons in granitic rocks. Each of these claims has been contradicted subsequently by other investigators. The statements are that:

1. Zircon in granites crystallized before any of the other constituent minerals.

2. Zircons of intrusive granites are euhedral and thus distinct from the rounded or fractured grains present in sediments.

3. Zircons of a granite pluton generally show some peculiarities of size, shape, or color which are the same throughout the body and by which the granite can be distinguished from its surroundings, other intrusions of different igneous rocks, or plutons of the same rock type of different ages.

4. Within the same tectonic belt, synchronous granite plutons contain zircons which show common characteristics of shape, size, or color throughout the belt, whereby such intrusions can be differentiated from asynchronous plutons in the same tectonic belt, or from both synchronous and asynchronous plutons in other tectonic belts.

Recognition of the Granite Series by Read (1951, 1955) and others has lent further interest to these claims. Only zircons in intrusive granites will be discussed here, while those in autochthonous and parautochthonous granites are more properly considered in the third paper of this series, dealing with zircon in metamorphic rocks.

Very little is known concerning zircon in igneous rocks other than granite, yet these other rocks should not be excluded from a survey of this type. Although data are not as abundant as is desirable, they allow certain tentative conclusions and focus attention on possible uses of zircon studies in petrogenetic problems.

## ACKNOWLEDGMENTS

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Eckelmann, L. H. Larsen, and R. E. Wilcox. He also gratefully acknowledges the help of several friends in collecting samples for this work, especially Mr. J. W. von Backström of the Geological Survey, South Africa, and Dr. L. T. Nicolayson of the Bernard Price Institute, South Africa. Dr. M. Fleischer of the U. S. Geological Survey, Washington, D. C., kindly gave the writer a summary of zirconium abundance data derived from unpublished analyses. Through the years the writer has benefited from many fruitful discussions and much stimulating correspondence with geologists here and overseas. These studies started at the Department of Geology, University of Cape Town, South Africa, under the writer's friend and mentor, Professor F. Walker, continued at the Geological Survey, Lobatsi, Bechuanaland Protectorate, under the then Director, Mr. E. J. Wayland, and finally at this University. Parts of the work were financed by the Kemp Memorial Fund and the Eugene Higgins Fund.

## ZIRCON IN BASALTIC ROCKS

Wager and Mitchell (1951, p. 192-193) and Nockolds and Mitchell (1948, p. 551, table 9) find that zirconium is concentrated in the pyroxene of basaltic rocks. Wager and Mitchell (1951, p. 192) interpret this concentration as indicating that zirconium forms part of the crystal lattice of magnesian pyroxenes of early crystallization. Hevesy and Würstlin (1934, p. 309) give the average zirconium content of gabbros as 140 p.p.m.. Fairbairn et al. (1953, p. 44) find a range of 1-270 p.p.m. zirconium in 59 Ontario diabases of different ages, while Fleischer (personal communication, 1954) gives a range of 10-1500 p.p.m., average 170 p.p.m. zirconium for 202 samples of igneous rocks with $SiO_2$ 45-55 percent.

Observations in the literature on zircon in basaltic rocks are relatively rare. Thürach (1884, p. 220) remarks of zircon concentrates in three basalts and one diabase: "Die mikroskopish kleinen Zirkone der Basalte sind fast stets stark abgerundet, so dass man nur selten scharfe Krystalle findet, aber diese abgerundete Beschaffenheit ist ihnen von Natur aus eigen, da die nicht seltene zonale Streifung der rundlichen Körner der äusseren Umrandung genau parallel läuft." He finds rounded zircons also in many other effusive rocks. The problem of apparent and real rounding of zircons in igneous rocks is discussed later. Thürach also mentions relatively large hyacinths found in several localities (e.g., Brauns, 1919), which he regards to be xenocrysts. Von Chrustschoff (1886a, p. 438) reports thin, nearly square, colorless zircons with sharply euhedral outlines in an apatite-rich basalt from Mexico. Groves (1927a, p. 248-250) describes euhedral zircons from two gabbros and a gabbro-pegmatite from the island of Jersey. Taylor and Gamba (1933, p. 368-369) state that on the Isle of Man an older gabbro intruded by the Oatland granite has euhedral zircons, commonly with irregular outlines due to corrosion. A hybrid monzonite produced by granitization of the gabbro at the contact with the Oatland granite has similar, strongly corroded zircons. Taylor (1934, p. 5) reports that the gabbro associated with the Mountsorrel granodiorite has small, clear, euhedral zircons of average size 0.09 x 0.04 mm, as well as "large irregular zircons showing little or no crystal form and often much fractured." Wilcox (1936) finds zircon needles up to 7¼ in. long,

of early crystallization, in a gabbro-pegmatite from Wisconsin. Frankel has drawings and a photograph (1943, pl. 7) of fractured and well rounded zircons from the Merensky Reef in the Bushveld Complex of South Africa. Feniak (1944, p. 419) gives the average size of zircons measured in thin sections of mafic igneous rocks as 0.057 x 0.035 mm.

The writer and his associates have examined zircon concentrates in the following basaltic rocks:

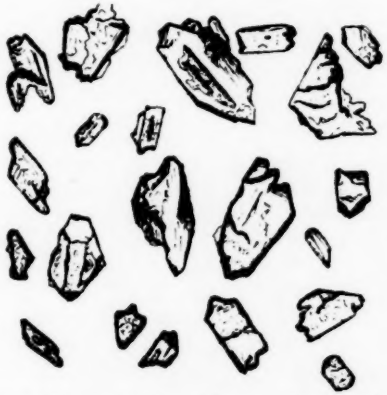

Fig. 1. Zircon in spilitic rocks, New Mexico (after Duschatko and Poldervaart, 1955). Magnification × 80.

*Spilitic rocks from an intrusion in New Mexico* (Duschatko and Poldervaart, 1955). Erratic distribution of zircons; many samples yield only a few crystals, others give poor crops of 100-300 zircons. The majority of the crystals (fig. 1) are jagged chips or irregular skeletal crystals, with only a few simple bipyramidal prisms. Crystals are small and short; crystal edges and points are sharp, while surfaces are smooth or striated.

*Upper Palisade diabase, New Jersey.* Poor zircon crops, again mainly minute, irregular or skeletal forms with rare, rather flat, euhedral crystals, none tabular.

*Gabbros of Bald Mountain batholith, Oregon* (Taubeneck, in press). Generally poor zircon recovery. Willow Lake norite has zircons of irregular form, together with a few subrounded individuals which, however, do not resemble sedimentary zircons. Badger Butte quartz-biotite norite has a majority of strikingly irregular fragments (fig. 2) and few euhedral crystals with elongations less than 2.0. Black Bear quartz gabbro has a minority of irregular forms; most zircons are prismatic, but with pyramidal terminations either lacking or present only at one extremity.

*Ortho-amphibolite, Roan Mountain, Tennessee.* Poor zircon crop; mainly irregular forms, including some rough, subrounded crystals and rare subhedral or euhedral zircons.

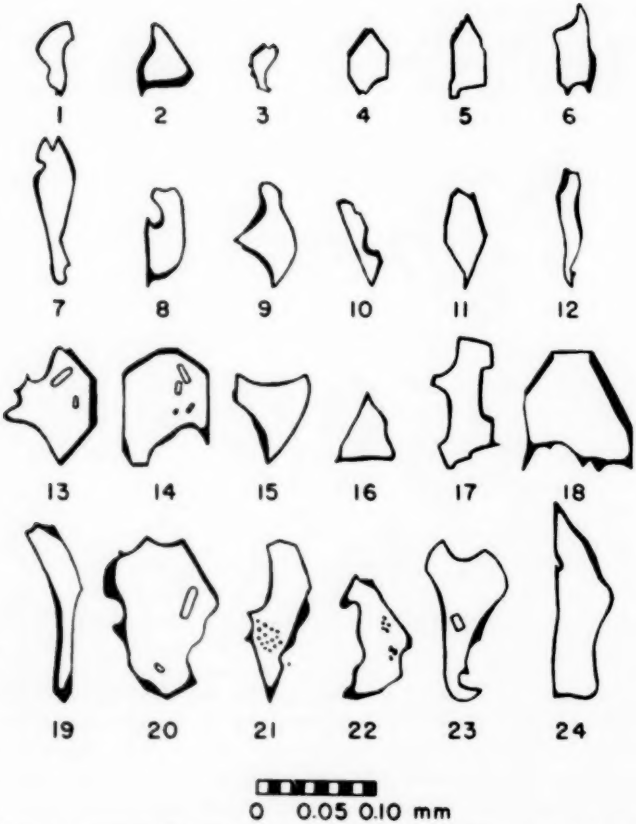


Fig. 2. Zircon in Badger Butte norite, Oregon (after Taubeneck, in press).

*Contaminated metabasaltic dikes, Keimoes, South Africa.* Poor zircon crops; many irregular forms or subhedral to euhedral crystals, also frequent well rounded grains with smooth surfaces.

Tests run in this laboratory indicate that mechanical breakage of zircons in crushing is less than 10 percent of total crystals present if their maximum diameter is less than 0.2 mm (Hoppe, 1951, p. 65).

Accordingly, the writer interprets the results obtained as indicating that:

1. Especially in more mafic basaltic rocks, and presumably also in ultramafic rocks, most of the zirconium occurs in the pyroxene lattice, and not as zircon.

2. In less mafic basaltic rocks, part of the zirconium is present as zircon crystallites with irregular forms.

3. In the crystallization sequence of basaltic magma, zircon is therefore regarded as a product of late crystallization. Since the temperature of basaltic

magma is 1125° ± 50° C. (Poldervaart and Hess, 1951, p. 478), and such magma is practically consolidated at 900° C. (Wager and Deer, 1939, p. 223), it seems likely that the crystallization range of zircon *in this environment and with these zirconium concentrations* is of the order of 900°-1000° C.

4. The late crystallization of zircon from basaltic magma may explain the striking differences in habits found (Wells, 1931, p. 261). However, generally there are also irregular crystallites present, although these may be interpreted erroneously as fractured or corroded crystals.

5. Some zircon concentrates with irregular or subrounded crystals may be difficult to distinguish from those of siltstones or shales, which contain considerable proportions of small, mechanically broken grains. Subrounded crystals may result from exsolution of zirconium initially in the pyroxene lattice.

6. Well rounded grains with smooth surfaces may well be xenocrysts, especially if their maximum diameter is greater than 0.1 mm. Smaller, rounded grains may have been corroded by the magma.

The main interest of zircon studies of basaltic rocks is in tracing magmatic differentiation, e.g., in the series basalt-trachyte-phonolite or the series basalt-granophyre, or in their application to studies of metasomatism or assimilation of country rocks by basaltic magma (Walker and Poldervaart, 1949, p. 674-684; Jansen, 1955). Detailed studies have not yet been made.

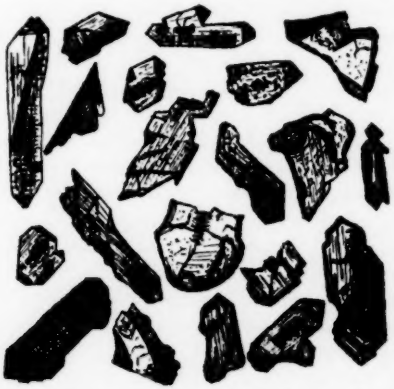

Fig. 3. Zircon in Dillsburg granophyre, Pennsylvania. Magnification × 80.

Granophyres associated with dolerite in a sheet near Dillsburg, Pennsylvania (Hotz, 1952, 1953), were examined by both Hotz and the writer. Hotz (1953, p. 684) reports that "the unbroken zircons all had sharp crystal terminations." Zircon concentrates obtained in this laboratory show a remarkable variety of crystal habits (fig. 3), including a majority of highly irregular, *seemingly* broken crystals, many with only one or two crystal faces, others of prismatic habit but without pyramidal terminations or so terminated at only one extremity, and a minority of sharply euhedral crystals. Many zircons are colorless, others pale brown and pleochroic, while yet others have

opaque cores or are completely black. There is some resemblance to the zircons obtained from the upper Palisade diabase and from albitites associated with spilitic rocks in New Mexico.

Tyler et al. (1940) examined zircon concentrates of middle Keweenawan granophyres similarly associated with diabase. They report that, in addition to euhedral crystals, there are zircons which have "a corroded appearance with jagged, serrated edges and a pitted, striated, and irregular surface. The grains have an irregular outline often vaguely suggesting prismatic form" (p. 1467). These authors suggest that such forms are "due to partial resorption of earlier-formed crystals, resulting in the irregular serrated grains" (p. 1468), but the present writer thinks it more likely that they represent early stages of growth. Serrated or jagged, angular shapes are more likely in early growth than in resorption which would tend to round-off rather than form or sustain irregular, sharp features.

Metasomatic granophyres and associated Karroo siltstones from the Rietkop sill (Walker and Poldervaart, 1949, p. 681; fig. 38) contain only a few minute zircon fragments.

## ZIRCON IN ALKALINE ROCKS

The zirconium content of alkaline rocks is roughly of the same order of magnitude as that of granites, but the highest zirconium values are reached in peralkaline rocks. Nockolds and Allen find that zirconium increases throughout the alkaline series (1954, p. 263), while in the calc-alkaline series it rises to a maximum, but decreases again in the extreme differentiates (1953, p. 138). Zircon is present in many alkaline rocks and yields are comparable to those obtained from granites, but some peralkaline rocks contain zircono silicates such as eudialyte, etc., in addition to or instead of zircon. Gerasimovsky (1941) suggests a classification of nepheline syenites into *miaskites*, with alumina:alkalies ratio greater than 1, and *agpaites*, in which this ratio is less than 1. Miaskites contain zircon, but agpaites are characterized by zircono silicates. However, nepheline syenites from the Mariupol area are agpaites, although some with relatively high $SiO_2$ contain zircon, while others with less $SiO_2$ have zircono silicates. Guimarães (1948, p. 78) is of the opinion that zircon has high initial stability but is dissociated by residual fluids with high concentrations of Na, F, and Cl.

The type rock *mariupolite* is described by Morozewicz (1902, 1930). It is characterized by small bipyramidal zircons, usually (111) with minor development of (221), and without prism faces. Similar bipyramidal zircons are found in foyaites and other syenites associated with the mariupolite, and the persistence of this unusual habit of zircon in all the alkaline rocks of the area is regarded by Morozewicz (1930, p. 422) as evidence of comagmatic origin. Larger zircons become common in certain phases of mariupolite, where they reach 5 mm in maximum diameter. These larger crystals are euhedral, but poikilitically enclose albite, while they are usually surrounded by "schlieren" of small, bipyramidal zircons (1930, pl. 16). According to Morozewicz (1902, p. 246), the order of crystallization includes considerable overlap between crystallization ranges of zircon and albite, aegirine, and

nepheline (see also Brögger, 1890, p. 101-115). Aegirine may contain significant amounts of zirconium in crystal solution (Rankama and Sahama, 1950, p. 565).

Thürach (1884, p. 214-215) describes zircons from four syenites. Yields are comparable with those obtained from granites. Generally the zircons are euhedral, but one syenite (Robschütz, near Plauen) is stated to have euhedral and rounded zircons. The Redwitz syenite is characterized by highly elongated crystals, similar to those of the nearby Luisenburg granite. Thürach (p. 218-219) also describes zircons from one porphyry, two trachytes, two phonolite-tuffs, and one phonolite. Crystals are variously stated to be mostly rounded, or rounded and euhedral, but one phonolite-tuff has sharply euhedral zircons. Von Chrustschoff (1886a, p. 437) reports euhedral zircons from a trachyte. Brögger (1890, p. a101-115) describes bipyramidal zircons from alkaline rocks in southern Norway. Parsons (1931) records giant zircons, up to 12 x 4 in. and weighing up to 15 lbs., in syenitic aplite from Ontario. Jenks (1934, p. 479) describes colorless, euhedral zircons from a syenitic stock in Maine, and finds that "the crystal habit and color are practically invariant" throughout this stock (see Marsden, 1935).

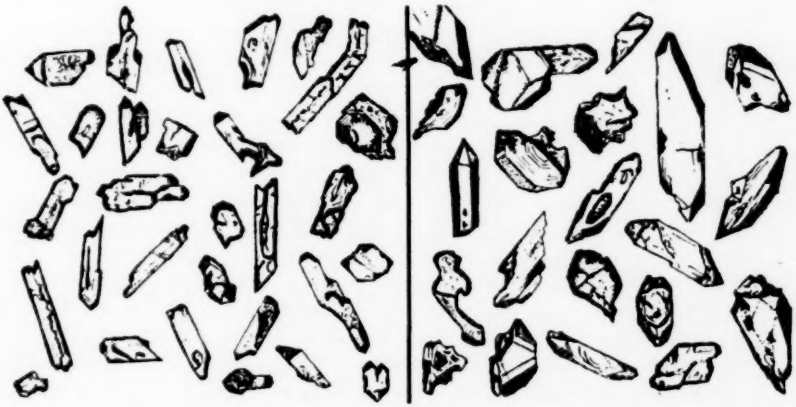

Fig. 4. Zircon in igneous albitites, New Mexico (after Duschatko and Poldervaart, 1955). Magnification × 80.

The writer has examined only a few mildly alkaline rocks. Dominion Reef alkaline porphyries from Korwe Hill, Bechuanaland Protectorate (Poldervaart, 1954, p. 319, 327) have small, euhedral zircons. Those (fig. 4) in albitites from New Mexico (Duschatko and Poldervaart, 1955) include skeletal forms and subhedral to euhedral crystals. Associated Yeso siltstones are locally albitized, but the zircons in the metasomatic albitites are rounded and have pitted surfaces, identical with those of the normal siltstones. There is no evidence of resorption of zircon by the sodic metasomatizing fluids. Alaskites from the Spruce Pine area (Eckelmann and Kulp, 1956), North Carolina, are extremely poor in zircon. Near Keimoes, South Africa, char-

nockitic adamellite-porphyry has been changed by pneumatolysis to syenites (von Backström and Poldervaart, 1953, in preparation), but these contain the same zircons as the adamellite-porphyries.

In some respects the size and shape distribution of zircons in alkaline rocks (miaskites) can be compared with that of zircons in granites, but there are problems specific to the alkaline clan which lend added interest to zircon studies of members of this series. Thus it would be of interest to investigate:

1. Series of nepheline syenites in which zircono silicates displace zircon as rock-formers. It might be expected that some nepheline syenites would have zircons showing strong resorption features, and indeed Morozewicz (1930) notes this in several rocks from the Mariupol area.

2. Alkaline differentiates of basalt magma which possibly betray their basaltic derivation in the shapes of their zircons and which might be distinguished on this basis from other alkaline rocks.

3. Alkaline ring-complexes; for example, zircon studies may prove useful in testing Daly's interpretation (1933, p. 511) of the Alnö Complex against that of von Eckermann (1948, 1950), or Shand's interpretation (1922) of the Spitskop Complex against that of Strauss and Truter (1951).

4. Alkaline rocks formed by partial melting of hornblende- or biotite-rich rocks (Bowen, 1928, p. 269-273; Waters, 1955, p. 715-717).

5. Valuable information concerning the stability of zircon in alkaline environments may also be gained from zircon studies of alkalinized granites (Strauss and Truter, 1951) and arenites (Larsen and Buie, 1941, p. 1834-1837).

## ZIRCON IN CALC-ALKALINE ROCKS

### *General Statement*

More work has been done on zircons in granitic rocks than any other type of igneous rock. Effusive and intrusive members of the diorite and granite clans are here discussed together, but differences between these rocks are noted. There is practically no information on zircons in andesites.

Useful reviews and listings of the literature are given by the U. S. National Research Council (1932-1938), Reed (1937), and Hoppe (1951). Many earlier papers give qualitative observations on zircons, e.g., their habits are described in general terms and concentrates are classified accordingly into crystals of various types which are stated to be common, less common, or rare; or zircons of one rock are said to be similar or dissimilar to those of another rock. Attempts to quantify these observations are few, nor is due consideration given to the rank of the rocks studied in the Granite Series. This is discussed below.

### *Abundance*

Nearly all the zirconium in calc-alkaline rocks is present as zircon. The zirconium content of granites varies greatly and accordingly there are many reports in the literature of different yields of zircon concentrates from different granites. On the Isle of Man good zircon crops are obtained from the Dhoon granite, but zircon is less abundant in the Oatland and Foxdale granites (Taylor and Gamba, 1933). In the Caledonian Shap granite of the

Lake District, zircon is distinctly rare (Rastall and Wilcockson, 1915), but in the Armorican granites of Devon, Cornwall (Brammall, 1928; Ghosh, 1928; Chatterjee, 1929; Leech, 1929), and Channel Islands (Groves, 1927a, 1927b, 1930), it is more abundant. Pabst (1938, p. 49-50) notes that the Taft granite is richer in zircon than any of the other granitic bodies in the Yosemite region.

Variations may also occur in zircon yields of granites from the same pluton, but usually differences are less marked. McAdams (1936, p. 130) reports that zircon is more abundant in one sample of Lone Grove granite than in others, while Quinn (1943) records settling of zircon in a granodiorite dike on Rhode Island. Hevesy and Würstlin (1934, p. 308-309) give the average zirconium content of diorites and granites as respectively 280 and 470 p.p.m., the range for granites being 70-2000 p.p.m. Fleischer (personal communication, 1954) notes that for 208 samples of igneous rocks with $SiO_2$ 55-65 percent, the range in zirconium content is 20-3000 p.p.m., the average being 177 p.p.m., while for 240 samples of igneous rocks with more than 65 percent $SiO_2$ the range is 4-3000 p.p.m., the average 204 p.p.m. In aplites the zirconium content drops sharply and recovery of zircons from such rocks is generally poor.

### *Euhedral versus Rounded Zircons*

Much has been written on the problem whether granites contain euhedral or rounded zircons.[1] A survey of the literature leaves a confused picture; for example, Winchell's statement (1914, p. 128) that "nearly all zircon in igneous rocks and their metamorphic equivalents is clear and sharply angular" is contradicted by Armstrong (1922). Mackie (1928, p. 25-26) finds that zircons in the more silicic Scottish granites show very close zoning and frequently have imperfect terminations, exhibiting "a general somewhat irregular rounding" (Rastall and Wilcockson, 1915). In synkinematic granites (the Rubislaw granite), many of the zircons are rounded or ovoid in shape, but in rocks in which metamorphism occurred after consolidation (the Inchbae granite), the zircons are not rounded. Bruce and Jewitt (1936, p. 208) conclude that the rounding of zircons in foliated granite and the sharpness of the forms in massive granite "are features that deserve more detailed study." Baker (1942, p. 208-209) notes that in more than a hundred granitic rocks from Victoria, Australia, most of the zircons are euhedral, and "rare rounded (water-worn) examples are probably xenocrysts." Various authors have also noted corroded forms in zircon concentrates (Reed and Gilluly, 1932; Boos and Boos, 1934; Wilson, 1937). Claus' remarks (1936, p. 12-25) are also pertinent.

The writer's observations lead to the following conclusions:

1. No reliable observations concerning the characters of zircons can be based on thin-section examinations of rocks. Zircons often appear well rounded in thin section (Armstrong, 1922, p. 392, fig. 9), although concentrates of the same specimen may contain only euhedral crystals.

[1] "Rounded" zircons are crystals with rounded terminations but not necessarily with small elongations.

TABLE 1

Variation of Elongation with Length of Zircons

Cape Town granite, South Africa

| | | Length (mm) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Elongation | Unsorted | 0.05-0.09 | 0.10-0.14 | 0.15-0.19 | 0.20-0.24 | 0.25-0.24 | 0.30-0.34 | 0.35 |
| 1.0-1.4 | 4 | 18 | 8 | 5 | 1 | — | — | — |
| 1.5-1.9 | 26 | 46 | 45 | 29 | 9 | 6 | — | — |
| 2.0-2.4 | 66 | 25 | 33 | 45 | 40 | 24 | 11 | 1 |
| 2.5-2.9 | 48 | 8 | 8 | 15 | 32 | 25 | 20 | 3 |
| 3.0-3.9 | 38 | 3 | 5 | 5 | 17 | 31 | 27 | 15 |
| 4.0-4.9 | 13 | — | 1 | 1 | 1 | 12 | 24 | 16 |
| 5.0 and over | 5 | — | — | — | — | 2 | 18 | 15 |
| Total zircons | 200 | 100 | 100 | 100 | 100 | 100 | 100 | 50 |

Pend Oreille tonalite, Idaho

| Elongation | Unsorted | 0.05 | 0.05-0.09 | 0.10-0.14 | 0.15-0.19 | 0.20-0.24 | 0.25-0.29 | 0.30 |
|---|---|---|---|---|---|---|---|---|
| 1.0-1.4 | 3 | 2 | 1 | — | — | 1 | — | — |
| 1.5-1.9 | 15 | 8 | 20 | 5 | 3 | 3 | — | — |
| 2.0-2.4 | 27 | 17 | 54 | 24 | 9 | 8 | 2 | 1 |
| 2.5-2.9 | 33 | 7 | 50 | 45 | 17 | 8 | 2 | 1 |
| 3.0-3.9 | 44 | 50 | 34 | 67 | 30 | 28 | 7 | 2 |
| 4.0-4.9 | 25 | 27 | 20 | 34 | 21 | 11 | 4 | 2 |
| 5.0 and over | 53 | 89 | 21 | 25 | 20 | 16 | 4 | — |
| Total zircons | 200 | 200 | 200 | 200 | 100 | 75 | 19 | 6 |

2. Particularly if several different bipyramids occur at terminations of zircons, crystals may appear rounded when seen with low powers of magnification, but such crystals are perfectly euhedral when higher powers of magnification are used (Mackie, 1928, p. 27).

3. In studying zircons in granitic rocks, the rank of the granite in the Granite Series needs to be qualified. In most true intrusive granites (Poldervaart, 1950, p. 574; Read, 1951, p. 21), the majority of the medium-sized and larger zircons ($L > 0.05$ mm) are euhedral. Small proportions ($< 10$ percent) of xenocrystic, rounded zircons with smooth or pitted surfaces may be encountered. In autochthonous and parautochthonous granites, and in migmatites, the zircons are frequently not euhedral.

4. A few intrusive granites have small zircons ($L < 0.05$ mm) with well rounded terminations, although crystals of larger size are sharply euhedral. Examples are the Cape granite at Cape Town, South Africa (Scholtz, 1947; Walker and Mathias, 1947), and the Pend Oreille pluton in northern Idaho. In the Cape granite the small, rounded zircons have smaller elongations ($L/B < 2.0$) than the larger, euhedral crystals (table 1). The granite is characterized by pinite pseudomorphs after cordierite and contains many partly digested xenoliths of Malmesbury shales and siltstones which also surround the batholith. Hence the smaller zircons may well be xenocrysts. In the Pend Oreille tonalite the small, rounded zircons have the same range of

elongations as the larger, euhedral crystals (table 1). Apatite is partly of late crystallization in this pluton and encloses many of these minute zircons. Although again there are many scattered xenoliths in the igneous rock, it does not seem likely that these small crystals are xenocrysts. It should be noted that the size distribution of rounded versus euhedral zircons in these granites is the reverse of that encountered in sediments (Poldervaart, 1955, p. 453, table 7).

5. Other intrusive granites, especially those which show evidence of strong hydrothermal activity (e.g., red or orange potassic granites with much fluorite, etc.), may contain dark brown or opaque, closely zoned, altered zircons which may have rounded outlines, often with small irregularities which give the crystals a somewhat ragged appearance under high powers of magnification. Such crystals often have a narrow, colorless outer shell of low-birefringent material. Granites may also contain sharply euhedral, brown or black zircons. Alteration of zircons is discussed below.

TABLE 2

Types of Zircons in Silicic Volcanics

| Index | Rounded | Euhedral | | |
|---|---|---|---|---|
| | | Stubby | Normal Prismatic | Long Prismatic |
| 1 | xx | xx | x | — |
| 2 | xx | xx | x | tr |
| 3 | x | xx | x | — |
| 4 | x | xx | x | — |
| 5 | xx | xx | x | — |
| 6 | x | xx | x | tr |
| 7 | x | xx | xx | xx |
| 8 | xx | xx | x | — |
| 9 | xx | xx | x | tr |
| 10 | xx | xx | x | — |

xx >10 per cent
x minor amounts
tr trace amounts
— absent

Index

1 Rhyolite glass, Marysvale, Utah
2 Banded rhyolite tuff, Marysvale, Utah
3 Rhyolite porphyry, Marysvale, Utah
4 Rhyolite, Kremnicka, Hungary
5 Rhyolite porphyry, Cruz Verde, Mexico
6 Rhyolite tuff, Utah
7 Rhyolite, Swakura-Yama, Ishikawa, Japan
8 Rhyolite, Yellowstone Park, Wyoming
9 Rhyolite, Silver City, Nevada
10 Dominion Reef Felsite, Lobatsi, Bechuanaland Protectorate

6. There may be a few intrusive granites in which corrosion has resulted in rounding of the majority of the zircons. So far the writer has not found such granites. However, it would appear that rounding in these zircons might be more pronounced in the smaller crystals than in the larger ones and thus some valid criteria might be found to distinguish such concentrates from sedimentary zircon crops. Rounding of zircons by magmatic corrosion seems to be far more common in effusive (table 2) than in intrusive rocks. Happily there seldom is a problem concerning the magmatic origin of lava flows.

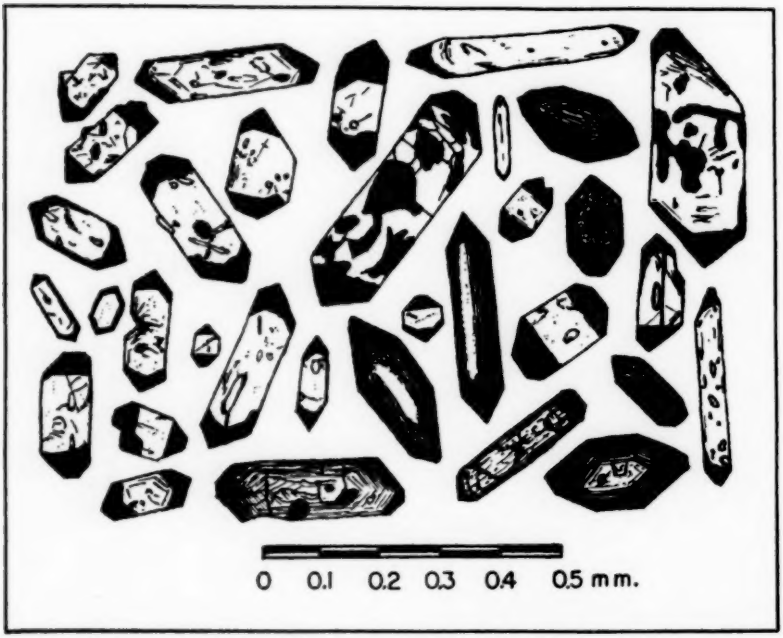


Fig. 5. Zircon in southern African granites.

To sum up, intrusive granites (sensu lato) normally contain a majority of euhedral zircons. Typical forms observed in southern African granites are shown in figure 5; other illustrations are given in many of the references cited in this paper. If special care is taken to recover also the minute zircons in these rocks, it may be found that the smaller crystals are rounded, but this is not always the case. In normal concentration procedures most of these smaller crystals are usually lost, and it may be better for comparative purposes to direct attention to crystals with $L > 0.05$ mm, which in sediments are more markedly rounded and in these igneous rocks more markedly euhedral. If high proportions of rounded zircons are found in intrusive granites, the rocks may be highly contaminated, the zircons may be brown or black and altered, or initially euhedral zircons may have been rounded by magmatic corrosion. Zircons in granites near contacts of younger dolerites have been observed to be slightly rounded or to have surface striations parallel to the *c* axis (von Chrustschoff, 1886b, p. 188; Tolman and Koch, 1936, p. 30).

### *Habit, Elongation, and Color*

Many attempts have been made to characterize granites by the habit, elongation, or color of their zircons. Zerndt (1927, p. 366, table 1) determines frequency percentages of different crystal faces developed in zircons of various

rocks. On this basis he finds that zircons of silicic effusives from the Krakow region are very similar to those of comagmatic granites from the Tatra Mountains. However, in the latter region, zircons from two massive granites on the same basis resemble the euhedral crystals in a gneiss which contains a majority of rounded zircons. Crystal faces counted by Zerndt are commonly developed in zircons from all granites, and hence this may not be the best method to characterize a particular granite. There are also practical difficulties in correct identification of particular faces in such minute crystals.

Taylor (1937, p. 689) remarks on the difficulty in deciding "which features should be selected for quantitative study: since there are generally some half a dozen or more—colour, size, crystal form, presence or absence of inclusions, zoning, etc.—all of which vary independently of one another." He divides euhedral zircons into four types with elongations roughly 1, $< 2$, 2-4, and $> 4$, and also recognizes a fifth type of anhedral crystals. The distribution of these types is studied in three granites at different levels of the Mourne Mountains Complex in northern Ireland. Taylor (p. 695) concludes: "It appears, therefore, that in the two intrusions most suitable for an investigation, there is quite an appreciable change in the character of the zircon between the highest and lowest samples collected. It must be remembered that in neither case was the vertical range more than 1000 feet and consequently one feels that in the comparison of separate but co-magnetic granites which have been eroded to levels differing by several thousand feet—as may frequently be the case—there are liable to be major differences in the habits of the zircons from the separate masses." Opposed to these observations are the conclusions of, for example, Groves (1930, p. 235) who remarks that "it will be found that the habit or habits of the zircon of any granite mass are fairly, and often very, regular throughout the mass and even when the mass is composite there is often a general community of aspect (as distinct from one particular habit)." Or of Reed and Gilluly (1932, p. 217) who state that zircons of biotite-quartz diorite samples from eastern Oregon, collected as much as 30 miles apart, "have similar development in size, proportions, and degree of perfection of crystal forms. The similarities are so marked that a single mount of the residues almost suffices to place the specimen in or out of this group." Or of Dapples (1940, p. 449-450) who finds in a quartz monzonite-porphyry laccolith in central Colorado that "despite the variation in percentage of the mineral constituents the habits of the various minerals remain consistently the same throughout the rock mass of Mt. Wheatstone. Zircon, for example, occurs always as grayish, stubby, or long slender crystals, and both types are terminated with bipyramidal faces whose surfaces appear slightly rounded. The persistence of occurrence of the same accessory minerals in the same habits is noteworthy and emphasizes the value of using peculiar habits, anomalous optical properties, characteristic colors and other like properties as a more reliable means than mineral percentages for correlation of igneous bodies." In a well controlled study of the Hirao granodiorite and Kaho granite, Karakida (1954) finds that color and crystal habit of zircons in each of these bodies are practically invariant. Mackie's careful statement of the problem (1928, p. 25) may be recalled: "It may be stated as a broad

generalization, to which there are few, if any, exceptions, that the zircons of any particular granite are of more than one . . . it may be of several distinct types, though one of those types . . . usually the one occurring in relatively greater abundance (but this is not invariably) may be taken as the typical zircon for that particular granite."

Feniak (1944, p. 419) gives the average size of zircons in intermediate and silicic igneous rocks as respectively 0.066 x 0.046 and 0.063 x 0.042 mm, from measurements on thin sections. Size-frequency data on zircon in granites are given by Claus (1936), Smithson (1939), Coetzee (1942a, 1942b), Mathias (1940), Vermaas (1949), Poldervaart and von Backström (1950), Hoppe (1951), Rao (1953), and Wyatt (1954), but these studies do not include examinations of a number of samples from the same pluton.

Color of zircons has been used frequently in attempts to characterize granites since Brammall (1928) found that the Dartmoor granite was distinct from other granites in the region in having an abundance of dusky zoned zircons. Chatterjee (1929, p. 149) tabulates the distinguishing characters of the Bodmin Moor, Falmouth, Dartmoor, and St. Austell granites, and again the main distinctions are those of color. Tyler et al. (1940) find in their studies of Lake Superior Precambrian rocks that early pre-Huronian granite and granite-gneiss contain purple hyacinths, late pre-Huronian and Huronian rocks have colorless and dirty yellow zircons, while Keweenawan rocks show colorless and pale yellow-brown crystals. Tyler (1940) also notes that the Precambrian rocks of the New Jersey Highlands are characterized by hyacinths, while the younger granite near Sing Sing contains malacons. Tomita (1954) uses color of zircons to distinguish Archean from younger rocks.

### *Classification*

Qualitative observations of the writer and his associates are summarized below.

In the majority of granites, the zircons show a range of similar features which makes it improbable that they can be characterized by qualitative observations alone. There is also danger that certain peculiarities are so conspicuous that an exaggerated impression is formed of their relative abundance in the concentrates. A few granites are characterized by the very wide range of shapes, sizes, colors, and other features shown by their zircons (e.g., the Dillsburg, Pa., granophyre). Others may have high proportions of zircons of unique characters which distinguish them from all other granites in the region (e.g., the Bugaj granite with about 11 percent of bipyramidal zircons without prism faces, described by Zerndt, 1927, p. 368). However, such granites are rare.

A relatively simple and rough classification of unmistakable and easily recognized zircon characters is more useful for identification purposes than excessively detailed classifications. Common zircon characters, encountered in most igneous rocks, are less useful for classification than are more unusual features. On the other hand, small significance can be attached to uncommon

characters of low relative abundance in the concentrates. A simple and easily adaptable scheme of zircon characters might be based on:

*Simplicity, complexity, or absence of terminal faces.*—In most granites, terminations are relatively simple in the majority of zircons, although a few crystals with complex terminations generally may be found. Granites with a majority of complexly terminated zircons are therefore satisfactorily characterized, but the presence of complexly terminated crystals in minor amounts in zircon crops cannot be regarded as diagnostic. In diorites the position seems to be reversed; the writer has seen more diorites with high proportions of complexly terminated zircons than with a predominance of simply terminated crystals. Most granites have a majority of doubly terminated zircons, but again a few granites may have high proportions of zircons terminated by crystal faces at only one end, or without any terminal faces. If crystals are large, this may be attributed to breakage in the laboratory, but if they are small it may be regarded as characteristic of the granite. Exact identification of terminal faces in zircons seems of dubious value as generally only the most common forms can be recognized with certainty (Claus, 1936, p. 13-14). However, recognition of certain relatively uncommon and easily identified terminal faces may be useful in classification, particularly if these forms are present in a high proportion of the crystals. Thus the basal pinacoid (001) may be absent, poorly developed, or prominent. Again, a very steep bipyramid (331) may be conspicuous in zircons with simple terminations.

*Elongation, rounding, and corrosion.*—Most granites have a majority of zircons with elongations 2.0-3.0; unusual in that respect are granites with relatively high proportions of stubby crystals ($L/B < 2.0$),[2] or of long-prismatic crystals ($L/B > 4.0$). Diorites seem to be somewhat different; the writer has seen more diorites with stubby zircons than with normally elongated or long-prismatic crystals. Yet the Pend Oreille tonalite has the most elongated zircons and the widest range of elongations encountered so far (L/B up to 32.0). A three-way classification into stubby, normally elongated, and long-prismatic zircons may be useful when applied to rocks in which such habits reach significant proportions. Rounding and corrosion have been discussed. Their value in classification is somewhat doubtful (see also Reed and Gilluly, 1932, p. 220).

3. *Color and inclusions.*—Color may be useful as a distinguishing feature if it is conspicuous and colored zircons are abundant in the concentrates. Many granites contain a few pale purple zircons, but relatively few granites have a majority of dark purple hyacinths. Generally pale colors are less useful than dark colors. Thus colorless zircons are not clearly distinguishable from the so-called "gray" crystals, and pale yellow, brown, or purple zircons are also less conspicuous and therefore less useful in classification. The writer has observed that hydrothermally altered granites may contain more brown or black zircons than less altered samples of the same pluton, which indicates that some care must be exercised in using color as basis for distinguishing

[2] The writer (1950, p. 574) has stated that zircons in granites have elongation-frequency maxima in excess of 2.0. This is not true of all intrusive granites but applies only to the majority of intrusive granites and apparently the minority of intrusive diorites.

granites. Deeply colored zircons often have opaque cores, but such features are rare and therefore more diagnostic in crystals with colorless mantles. Most zircons have a few inclusions and colored zircons often have many inclusions. However, colorless zircons riddled with inclusions are relatively uncommon in granites (though apparently more common in diorites), and this feature can therefore be used as a distinguishing mark. Brown zircons are frequently zoned; colored crystals are often cracked (Hutton, 1950, p. 695-697). Hence these characters may not have great diagnostic value.

A detailed classification scheme was tested by the writer on 10 graduate students, using 20 concentrates. Checks of their results showed numerous inconsistencies in the less conspicuous zircon characters, and in features present only in minor amounts. Simplification of the results to include only conspicuous characters, developed in significant proportions of the zircons, brought the group in accord. Results according to this simplified scheme are shown in table 3. The writer contends that more detailed identification of the concentrates is possible (i.e., reproducible) only when actual counts and measurements are made.

It is clear from this table that only a few granites in this group stand out as having zircons of unique characters. The Gaberones granite is unlike any other granite in the group in having relatively large, dark purple, pleochroic hyacinths of simple prismatic habit with conspicuous development of the basal pinacoid. The Cape Town granite is also distinct; like the Salem and Spitzkoppe granites, the zircons are long-prismatic, but they are generally well terminated and the steep bipyramid (331) is conspicuous. The table also shows that correlation of granites on the basis of their zircons *only* may be misleading. The Karroo granite of Gross Spitzkoppe and that of the adjacent Klein Spitzkoppe (probably one pluton) are both characterized by long-prismatic, colorless or brown zircons with frequent black cores, and often without terminal faces or so terminated at only one end.[3] The Karroo granite from the Messum volcano 60 miles to the west-northwest of the Spitzkoppe granites (Korn and Martin, 1955) has quite different zircons, but the Proterozoic (?) Salem granite (Gevers, 1935, p. 240), an equal distance to the east-northeast, has very similar zircons. On the other hand, two Karroo granophyres from the Lebombo Belt in Swaziland have significantly different zircons. The rock with purple and brown zircons has a high magnetite content, while the one with colorless and a few pale purple crystals (riddled with inclusions and showing corrosion) is low in magnetite.

Strauss and Truter (1945) suggest that the Bushveld granite consists of three separate phases emplaced at different times. It is evident from the table that the three phases have similar zircons. Vermaas (1949) has shown that some of the Bushveld granites are recrystallized Rooiberg felsites and granitized country rocks and contain zircons with later-developed overgrowths. Such rocks might be grouped with the autochthonous and parautochthonous granites.

[3] It is noteworthy that the zircons of the Spitzkoppe granites show strong resemblances with those of some gabbroic rocks (e.g., Black Bear quartz gabbro of Bald Mountain batholith, Oregon) and certain basaltic differentiates (e.g., Dillsburg, Pa., granophyre, or New Mexico albitites).

Tomita (1954) has compiled a standard set of colored zircons which he uses to classify granites. He maintains that, seen in reflected light, purple or pink zircons are found only in Archean granites; younger rocks may have purplish brown zircons. The writer has examined zircons only in transmitted light, in which medium he has not been able to distinguish the pale purple zircons of some Karroo granophyres of the Lebombo Belt from those of Archean and Proterozoic granites in southern Africa. Colorless and brown zircons may occur in rocks of all ages. Wilson (1950) advocates study of zircons in ultraviolet light (2537 Å) as an aid in classification, both in the field and the laboratory. Judging from his results this method might prove useful in petrologic research.

### *Zircon Measurements*

Table 4 shows the distribution of elongations of zircons in some of these granites. Again it is evident that in most granites about half the zircons have elongations 2.0-3.0, but in diorites and silicic volcanic rocks there may be more zircons with smaller elongations. More detailed observations are available for a few granites.

*The Gaberones granite.*—Specimens of the two exposures of the gray, rapakivitic Gaberones granite (Poldervaart, 1954) all have a majority of the characteristic hyacinths described above. In addition the concentrates show a minority of opaque crystals. Along an estimated 250 miles the Gaberones granite is in contact with Dominion Reef felsites and along the contact a wide zone of pink to red, granophyric, non-rapakivitic granite is found. This granite is completely gradational into the felsites. The latter contain colorless or brown zircons, many of which are stubby or rounded. The granophyric granites have the same zircons as the felsites, completely different from those of the rapakivi granites. It is concluded that the Gaberones rapakivi granite is an intrusive granite, but the granophyric granites are recrystallized (and in places mobilized) equivalents of the Dominion Reef felsites. Added interest is given these features by the fact that on the farm Vanggatbult in the Union of South Africa, Black Reef quartzite unconformably overlies the granophyric granite, but at Mochaneng in the Bechuanaland Protectorate, the granite intrudes the Transvaal Dolomite. Since the Gaberones granite is intruded by Bushveld dolerite sills and dikes, the writer regards it as part of the Bushveld cycle of igneous activity, emplaced before the Bushveld norite, but Truter (1950, p. lvi), on the evidence of the "cold" contact with Black Reef quartzite, considers the granite pre-Transvaal. Perhaps the post-Pongola Mooihoek pluton in Swaziland (Hamilton, 1939, p. 68-70) is of the same age as the Gaberones granite.

*The Mahalapye granite.*—This granite (Poldervaart and Green, 1954, p. 62) is regarded as an autochthonous to parautochthonous, rather than an intrusive granite. Apparently it corresponds with the Palala granite (Truter, 1950, p. lvi) across the border in the Union of South Africa. Zircons of the normal granite show high proportions of brown crystals (malacons) and minor amounts of colorless crystals. Terminations in most of the zircons are complex, and many crystals show rounded cores surrounded by subhedral or

TABLE 3
Classification of Zircons of Some Granitic Rocks

| | N | N | N | P | CS | CS | CS | CS | CS | P | VB | KK | PJR | CS | P | PJR | PJR | T | N | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Index | 69 | 50 | 64 | 270 | 451b | 483 | 922 | 541 | 518 | 10 | 1 | 43 | 215 | 256 | 337 | 373 | 370 | 9 | 464 | 626 |
| A. Terminations | | | | | | | | | | | | | | | | | | | | |
| 1. Simple | xxx | xxx | xxx | x | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xx | xxx | xxx | xxx | xxx | xxx |
| 2. Complex | x | x | x | xxx | x | x | x | xx | x | — | x | x | x | x | xxx | — | — | — | x | x |
| 3. One end only | — | xx | — | — | — | — | — | — | — | — | — | — | xx | — | — | xx | xx | — | — | xx |
| 4. (001) developed | x | x | x | xx | xx | xx | x | xx | x | xxx | — | — | — | xx | — | — | — | xx | xx | x |
| 5. (331) developed | — | — | — | — | — | — | — | — | — | — | — | — | — | — | xxx | — | — | — | — | — |
| 6. Rounded | x | x | — | xx | — | — | x | x | x | — | x | x | x | — | — | x | — | — | — | — |
| B. Shape | | | | | | | | | | | | | | | | | | | | |
| 1. Stubby | x | x | xx | xx | xx | xx | xx | xxx | xx | xx | xx | x | x | x | x | — | — | xxx | — | x |
| 2. Normal-prismatic | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xx | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xxx |
| 3. Long-prismatic | — | — | — | — | — | — | — | — | — | x | — | — | xx | x | xx | xx | xx | — | — | — |
| C. Color | | | | | | | | | | | | | | | | | | | | |
| 1. Colorless | xxx | — | — | x | x | x | x | x | x | — | xxx | xx | xxx | xxx | xxx | xxx | xxx | xxx | — | xxx |
| 2. Brown | xx | xx | xxx | xxx | xxx | xx | xxx | xxx | xx | x | xx | xxx | xx | — | xx | xx | xx | x | xxx | — |
| 3. Purple | — | xxx | — | xx | xx | xxx | xx | xx | xxx | xxx | — | x | — | xx | — | — | — | — | xx | x |
| 4. Black | — | — | xx | — | — | — | — | — | — | x | — | — | — | — | — | x | x | — | — | — |
| 5. Zoned | — | x | xx | xx | xx | x | x | x | x | x | x | x | — | — | — | — | — | — | x | — |
| D. Other characters | | | | | | | | | | | | | | | | | | | | |
| 1. Colorless crystals with black cores | — | — | — | — | — | — | — | — | — | — | — | — | xx | — | — | xxx | xxx | — | — | — |
| 2. Colorless crystals with many inclusions | — | — | — | — | — | — | — | — | — | — | — | — | — | xxx | — | — | — | xxx | — | xxx |

xxx Abundant
xx Significant proportions
x Small proportions
— Absent or rare

*Precambrian granites*

N 69 Kafue granite, Northern Rhodesia (Guernsey, 1950).

N 50 Bikita granite, Southern Rhodesia (Tyndale-Biscoe, 1951).

N 64 Matopo granite, Southern Rhodesia (Amm, 1940).

P 270 Mahalapye granite, Bechuanaland Protectorate (Poldervaart and Green, 1954).

CS 451b Red Bushveld granite (type 1), Zaaiplaats, South Africa (Strauss and Truter, 1945).

CS 483 Gray Bushveld granite (type 2), Zaaiplaats, South Africa (ibid).

CS 922 Transitional Bushveld granite, Leeuwpoort, South Africa (ibid).

CS 541 Bushveld granite (type 2), dike in norite, Mooihoek, South Africa (ibid).

CS 581 Bushveld granite (type 2), Sterkwater, South Africa (ibid).

P 10 Gaberones rapakivi granite, Bechuanaland Protectorate (Poldervaart, 1954).

VB 1 Gray gneiss, Goodhouse, South Africa (Coetzee, 1942a).

KK 43 Gray gneiss, Kakamas, South Africa (Poldervaart and von Backström, 1950).

PJR 215 Salem granite, South-West Africa (Gevers, 1935).

CS 256 Kuboos granite, Doodskloof, South Africa (Scholtz, 1947).

P 337 Cape Town granite, Cape Town, South Africa (Walker and Mathias, 1947).

*Karroo granites*

PJR 373 Gross Spitzkoppe granite, South-West Africa.

PJR 370 Klein Spitzkoppe granite, South-West Africa.

T 9 Messum granite, South-West Africa (Korn and Martin, 1955).

N 464 Lebombo granophyre, Mananga, Swaziland.

N 626 Lebombo granophyre, Stegi, Swaziland.

TABLE 4

Measured Zircon Elongations in Some Granitic Rocks

| Sample | No. Zircons | Elongation | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1.0-1.4 | 1.5-1.9 | 2.0-2.9 | 3.0-3.9 | 4.0-4.9 | >5.0 |
| 1. Kafue granite, Northern Rhodesia | 200 | 17 | 32 | 129 | 19 | 2 | 1 |
| 2. Bikita granite, Southern Rhodesia | 200 | 5 | 43 | 118 | 30 | 4 | — |
| 3. Matopo granite, Southern Rhodesia | 175 | 10 | 73 | 85 | 6 | — | 1 |
| 4. Mahalapye granite, Bechuanaland Prot. | 200 | 19 | 75 | 90 | 16 | — | — |
| 5. Bushveld granite, South Africa | 200 | 28 | 75 | 92 | 5 | — | — |
| 6. Gaberones granite, Bechuanaland Prot. | 200 | 10 | 58 | 119 | 13 | — | — |
| 7. Gray gneiss, Kakamas, South Africa | 200 | 2 | 40 | 127 | 27 | 4 | — |
| 8. Salem granite, South-West Africa | 200 | 5 | 27 | 100 | 43 | 17 | 8 |
| 9. Kuboos granite, South Africa | 200 | 21 | 49 | 101 | 19 | 8 | 2 |
| 10. Cape Town granite, South Africa | 200 | 4 | 26 | 114 | 38 | 13 | 5 |
| 11. Messum granite, South-West Africa | 200 | 23 | 63 | 102 | 10 | 2 | — |
| 12. Lebombo granophyre, Swaziland Prot. | 200 | 14 | 44 | 121 | 20 | 1 | — |

euhedral shells. Most of the zircons are stubby. A microgranite dike in the Mahalapye granite has zircons of significantly different characters. Crystals are purple, brown or opaque, rounded cores are rare, terminations are simple, and many are normally elongated. Corrosion is evident in many of the crystals. In figure 6 zircon size-frequency curves are given for the normal

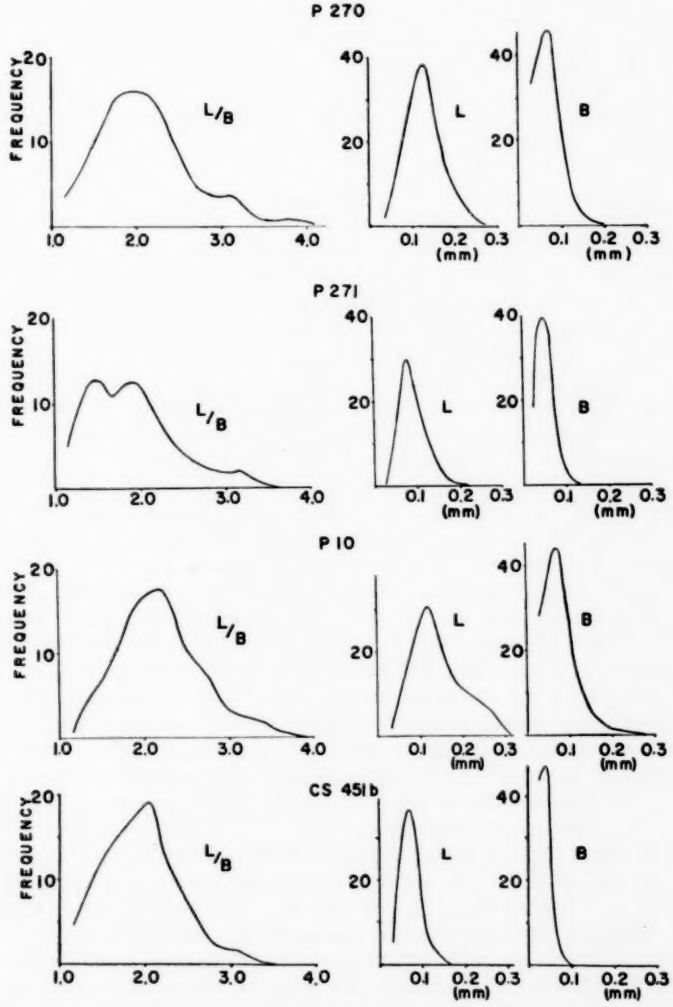


Fig. 6. Zircon size-frequency curves (200 crystals each sample). P 270—Mahalapye granite. P 271—Later microgranite dike in Mahalapye granite; P 10—Gaberones rapakivi granite. CS 451b—Red Bushveld "main" granite (type 1).

Mahalapye granite, the microgranite dike, the Gaberones granite, and the "main" Bushveld granite. Most likely possibilities are that the microgranite is: (1) a member of the Mahalapye Granite Series of higher rank than the normal granite, (2) a phase of the Gaberones granite, 100 miles to the south, or (3) a phase of the Bushveld granite, 80 miles to the east-southeast.

*The Cape Town granite.*—This granite (Scholtz, 1947; Walker and Mathias, 1947) can be distinguished from all other southern African granites by the long-prismatic habit of many of its zircons (tables 1, 3) and the steep bipyramidal terminations developed in a large proportion of the crystals. It is emphasized that not all the zircons are long-prismatic, nor do all show the unusually steep terminal faces. Although no actual counts have been made, specimens from various parts of the Cape Town batholith indicate that the main granite phase everywhere in the pluton shows these characters. However, the impression is formed that proportions of zircons with these habits may differ somewhat in different parts of the batholith. It is not known whether differences are sufficiently marked to affect the statistical distribution of zircon dimensions in the samples, i.e., whether zircon size-frequency curves will be significantly different in different samples. Generally there is good agreement between the writer's measurements and those of Coetzee (1942b).

Samples from other plutons of Cape granite have also been examined. Most of these contain zircons of the same characteristic habits as those of the Cape Town granite, though apparently in significantly different proportions. Some have only minor zircons of long-prismatic habit, and with these steep terminations. A few have no zircons which correspond to those considered characteristic of the Cape Town granite. This might be considered surprising if the Cape granites are believed to have been derived from one huge magma chamber but seems only normal when granite is considered in conformity with modern ideas concerning the Granite Series.

*The charnockitic adamellite-porphyry of the Keimoes district.*—This remarkable rock is found in several large phacoliths emplaced in Basement gneisses along the Orange River at Keimoes (von Backström and Poldervaart, 1953, in preparation). Detailed field and laboratory investigations have convinced the writer that the peculiar characters of these rocks result from contamination of a basaltic magma by silicic Basement rocks, mainly at depth. Zircon concentrates of samples from one of the phacoliths include both euhedral and rounded (or corroded) crystals. Figure 7 shows zircon size-frequency curves for four samples of different grain-size and up to 5 miles apart. The similarity of the curves is striking. All four samples have elongation-frequency curves with a primary maximum at 1.35-1.50 and a secondary maximum at 1.95-2.10. For one sample, separate curves are shown for 100 euhedral and 100 rounded or corroded zircons. The elongation-frequency curve for the euhedral crystals again shows the two maxima at 1.50 and 2.05. Probably the peaks are to be attributed to the development of (001) in about 40 percent of the euhedral crystals. However, the elongation-frequency curve for the rounded crystals shows the same two maxima. Similarities between the frequency curves of the euhedral and rounded zircons may indicate that the majority of the latter are not xenocrystic but are corroded or subhedral

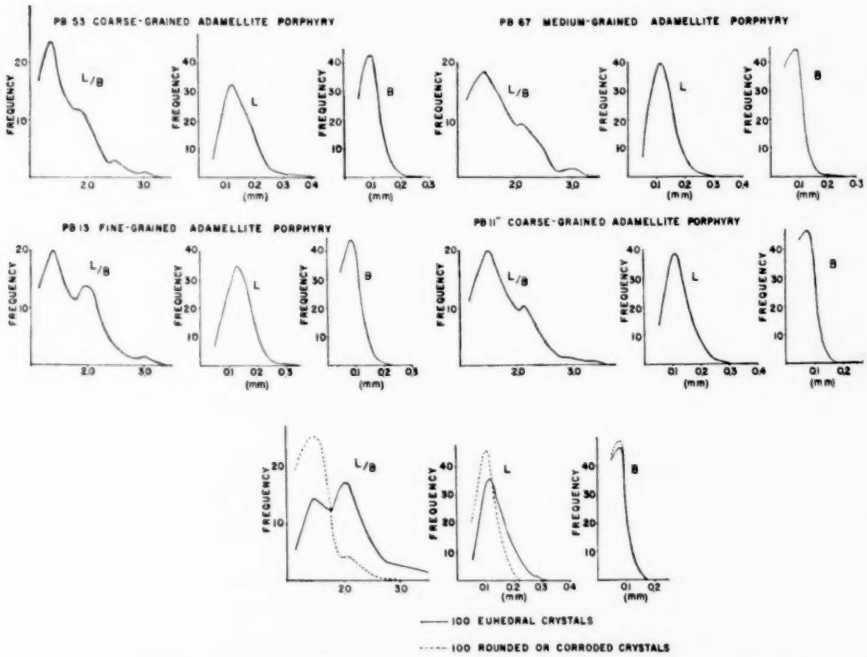


Fig. 7. Zircon size-frequency curves of Keimoes charnockitic adamellite-porphyry (200 crystals each sample).

forms crystallized as a result of supersaturation. The frequency curves of the rounded zircons also do not resemble those of the pink gneiss which is the predominant country rock in this region (Poldervaart and von Backström, 1950). Most significant is the observation that geographically widely separated samples within one intrusion of adamellite-porphyry yield zircon crops which are not only qualitatively indistinguishable but also yield the same or closely similar results upon measuring 200 crystals for each sample.

*The Hanover-Fierro intrusive, Grant Co., New Mexico.*—Specimens of this small granodiorite body (Hemon et al., 1953), 3 miles long by 1 mile wide, have been examined by C. Belt in this laboratory. Zircon crops show a preponderance of euhedral, colorless, simply terminated, stubby or normally elongated crystals; zircons are in fact those usually found in dioritic rocks. Figure 8 shows zircon size-frequency curves for four samples from different localities. The two porphyritic granodiorites are practically identical, as are the two non-porphyritic granodiorites. However, when the two pairs of rocks are compared, minor differences are evident. Although the peaks of the various curves are approximately the same, larger numbers of zircons show greater range in elongation in the non-porphyritic than in the porphyritic granodiorites. C. Belt is of the opinion that the porphyritic rocks have dif-

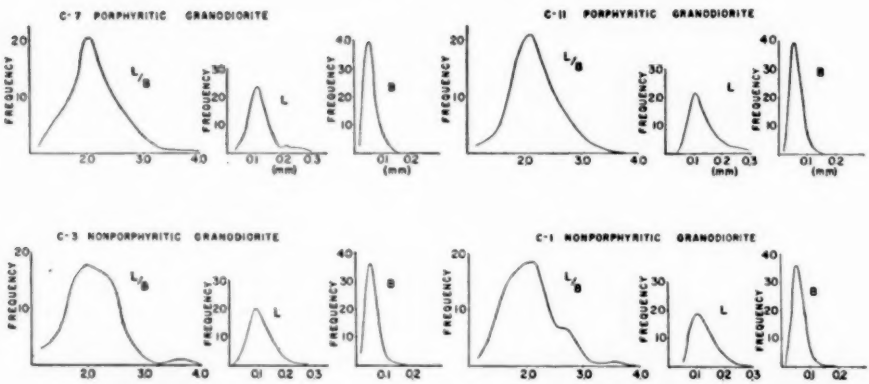


Fig. 8. Zircon size-frequency curves of Hanover-Fierro granodiorite, New Mexico. After C. Belt (200 crystals each sample).

ferentiated from the non-porphyritic varieties, since phenocrysts in the former are of the same composition as the constituent minerals in the latter. Differences in the zircon curves may therefore be the result of slight sorting upon differentiation.

*The Bald Mountain batholith, Oregon.*—Samples from this pluton have been studied by W. H. Taubeneck in this laboratory. The batholithic rocks vary from tonalite in the outer portions to granodiorite in the core of the pluton. In addition there are a few later intrusions of granodiorite and quartz monzonite which show sharp intrusive contacts against the main batholithic phases. Zircons of the main batholithic phases are again those usually found in dioritic rocks, but those of the later intrusions include more normally elongated and long-prismatic crystals. Figure 9 shows zircon size-frequency curves for three samples of the main tonalite-granodiorite and two samples of the later intrusive rocks. It is evident that the zircon crops of the batholithic tonalite-granodiorite are identical in spite of considerable petrographic differences (e.g., from 0.7 percent by volume K-feldspar in the border tonalite, to 7.9 percent in the granodiorite of the core). The zircons of the later intrusions resemble one another but are different from those of the main batholithic rocks. This is interpreted by the writer to indicate that the later intrusions are not derivatives of the same magma as the batholithic tonalite-granodiorite.

*Pegmatites from Greenwood, Maine.*—J. S. Cummings has examined zircons of a potassic and a sodic pegmatite from Greenwood, Maine, in this laboratory. Both pegmatites have a majority of euhedral zircons with minor amounts of rounded crystals. Figure 10 shows zircon size-frequency curves for two samples of sodic pegmatite and two of potassic pegmatite. All four samples are characterized by the unusually wide range of elongations of their zircons, especially pronounced in the sodic pegmatite. The two samples of sodic pegmatite have dissimilar elongation-frequency curves but closely similar

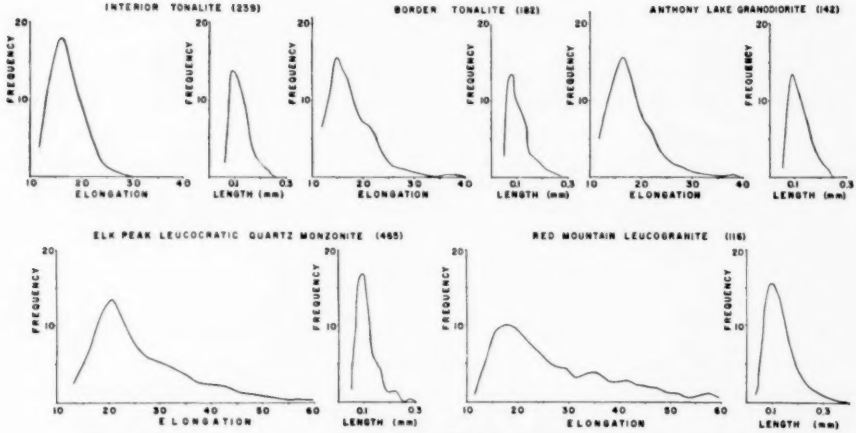


Fig. 9. Zircon size-frequency curves of Bald Mountain tonalite-granodiorite and later intrusives, Oregon. After W. H. Taubeneck (300 crystals each sample).

length- and breadth-frequency curves. The two samples of potassic pegmatite have identical zircon size-frequency curves.

The above examples indicate that zircon studies are more useful in petrogenetic investigations than in attempts to correlate granites. Sediments filling a geosyncline may be the same over considerable distances; in that case the granites which may eventually form from these sediments may have zircons of similar characters. On the other hand, the sedimentary fill may vary from place to place along the geosyncline; in that case the granites may have zircons of dissimilar characters. Again, there seems to be no reason why granites formed in mobile belts would have the same zircons as synchronous granites or rhyolites originating in adjacent "stable" portions of the continental crust. There is also danger in comparing zircon concentrates of different granites that similarities are emphasized which exist in zircons of most granites (e.g., prismatic habit, presence of (111), lack of color, etc.). On this basis Archean granites might be correlated with Tertiary granites.

On the other hand, the results obtained seem to the writer to be of some petrogenetic significance. There is no difficulty in identifying intrusive granites in terranes of low regional metamorphic grade (Read, 1951, p. 9-10; 1955, p. 419-421), but this problem does occur in granites encountered in areas of high metamorphic grade. Zircon studies are exceedingly useful in distinguishing intrusive from parautochthonous and autochthonous granites in such regions. Since zircons in a granite pluton are the same or closely similar in different parts of the body, granitized or contaminated portions of the pluton can be distinguished from normal magmatic phases (see also Karakida, 1954). In complex batholiths, zircon studies are useful in distinguishing differentiates of the same magma from rocks formed from different magmas at different times. The assumption is made frequently in petrology that all the rocks in complex batholiths (and nearly all large batholiths are complex)

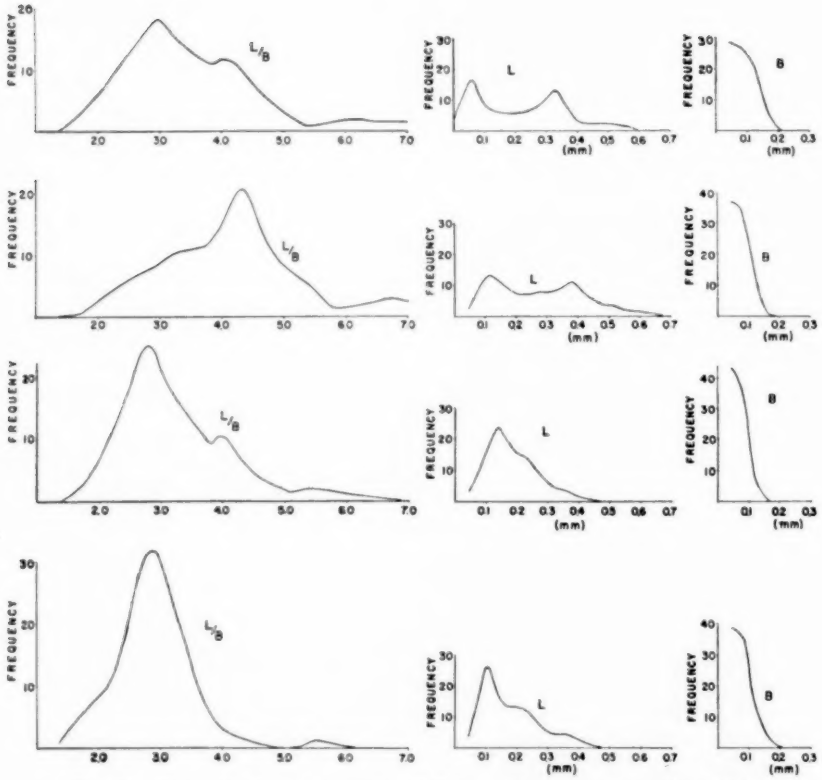


Fig. 10. Zircon size-frequency curves of Greenwood, Maine, pegmatites. After J. S. Cummings. P-S—Sodic pegmatite. P-K—Potassic pegmatite.

are derived from the same magma; this assumption needs investigation. There are countless other applications of zircon studies in problems of igneous petrology.

So far we have used a somewhat crude system of qualitative classification of zircons and more reliable size-frequency curves, determined by measurement of 200 unbroken crystals. However, our investigations have pointed up a need for more rigid statistical treatment of the data which will allow the computation of a "growth curve" for the zircons of a concentrate, characteristic of that concentrate. Such methods have been used by paleontologists for some time (Imbrie, 1955, 1956), and methods best adapted to the evaluation of zircon data are now being tested.

### *Crystallization of Zircon in Granite Magma*

The early literature indicates general conviction that zircon is one of the earliest minerals to crystallize from dioritic and granitic magma. The basis

for this opinion is probably the high melting point of zircon (2550°C.). However, recently zircon has been synthesized at temperatures as low as 240°C. (Frondel and Collette, 1953, p. 23). Evidence of late crystallization of zircon in many nepheline syenites has gradually changed earlier opinions, until it has become an open question whether or not zircon is of early crystallization in intermediate and silicic calc-alkaline magmas.

Quite apart from studies such as that of Gillson (1925), several investigators (Moorhouse, 1953) favor late crystallization of zircon from their examination of thin sections. Thus it has been noted that there is a decided concentration of zircons included in those minerals (especially biotite), which formed late in the crystallization sequence. In metamorphic rocks it may also be observed that zircon is preferentially associated with biotite, hornblende, and opaque ores, rather than with quartz and feldspars. To the writer this does not seem to be a valid argument for late crystallization of zircon. First, it seems likely that, even if zircon is of early crystallization, fewer zircons would be enclosed in free-growing crystals of early major constituents than in crystals which form late and are subject to mutual interference. Zircons trapped between such competing crystals would have to be included in one crystal or the other. Hence it seems more to the point to establish, if possible, that zircons are *absent* in the major constituents of early formation, than to emphasize their concentration in those of late formation. Second, it is entirely possible that zircons serve as centers of nucleation for ferromagnesian minerals, rather than for quartz and feldspars (Ramberg, 1952a; 1952b, p. 225). It should be noted that the production of a zirconium-rich zone (*geochemical culmination* according to Reynolds, 1946, p. 392) along contacts or xenoliths (Gillson, 1925; Karakida, 1954; Wyatt, 1954) also does not prove late crystallization of zircon. Possibly these zones are present only if contamination occurred early in the consolidation of magma, and thus zircon studies may provide guides to the time of contamination.

Wells (1931, p. 258-262) has pointed out the unlikelihood of a mineral of late crystallization being of the same size, shape, and color throughout a large igneous body. This argument could also be used in reverse. Considering the dependence of crystal growth on physical and chemical environment, it is unlikely that the same or closely similar crystals would be produced, *unless* the environment is remarkably uniform throughout the pluton. This uniform environment can reasonably be expected to exist only at the onset of crystallization. Thus the writer believes that most convincing evidence of early crystallization of zircon is found in the demonstrated uniformity of crystals throughout each of several igneous bodies. He has also examined thin sections of the rocks and has found in each case that zircon is also enclosed in the minerals of early formation, though often more zircons are included in those of late crystallization. Volcanic glasses have also been crushed in this laboratory, and in each case zircons have been separated from them, although yields vary greatly.

It was concluded that the crystallization range of zircon in basaltic magma is probably 900-1000°C. That of zircon in dioritic magma may well be of the order of 700-800°C., and in granitic magma 600-700°C. This tem-

perature range seems to be in agreement, both with the apparent early crystallization of zircon in such magmas, and with observations of marked corrosion and rounding of crystals in corresponding volcanic rocks.

TABLE 5
Physical Properties and Color of Zircon
(after Morgan and Auer, 1941)

| Color | $\omega$ | $\varepsilon$ | $\varepsilon - \omega$ | Radioactivity |
|---|---|---|---|---|
| Normal | 1.924-1.934 | 1.970-1.977 | 0.036-0.053 | low |
| Hyacinth | 1.903-1.927 | 1.921-1.970 | 0.017-0.043 | medium |
| Malacon | 1.782-1.864 | 1.827-1.872 | nil-0.008 | high |

*Malacons*

Brown and opaque zircons are usually called malacons. Morgan and Auer (1941) note that differences in color of zircon are associated with differences in physical properties (table 5).

Claus (1936, p. 25) has found that there are two types of brown or opaque zircons: (1) altered zircons with dull luster and frequently with rounded outlines, and (2) metamict zircons with bright luster and sharply euhedral outlines. Both types are hydrated (Frondel, 1953), have low birefringence, and lower densities than colorless zircons. Both may have thin, clear outer shells of low birefringence. Tested on photographic plates, the metamict zircons are highly radioactive, the altered zircons are not. Claus concludes that hydrothermal alteration may produce malacons.

The writer's observations tend to support Claus' results. There seem to be two types of brown or opaque zircons, one of which (dull luster, rounded outlines) is found preferentially in red granite phases (table 3). However, it is not true that all hydrothermally altered granites contain such alteration malacons. Additional factors to be considered are probably time of alteration and temperature of hydrothermal solutions. These observations are also in keeping with the occurrence of malacons in argillites (Poldervaart, 1955, p. 443).

*Long-prismatic Zircons*

Granites with abnormally elongated zircons have intrigued several petrologists. Rocks with a few crystals with elongations much in excess of 4.0 are not too uncommon, but those with significant proportions of such long-prismatic zircons are distinctly unusual. Quite naturally, attempts have been made to interpret this habit in terms of environment and conditions during growth of these crystals. Thus Mackie (1928, p. 26) thinks that long fine needles of zircon "represent the residual zircon substance crystallizing—in the last stage of consolidation." Claus (1936, p. 22-23) attributes this habit of zircons to pronounced under-cooling, Hoppe (1951, p. 97-98) invokes rapid cooling or low viscosity, while Wyatt (1954, p. 988) finds that elongated zircons characterize contaminated granites.

As yet there is little experimental information to guide enquiries of prevalence of particular crystal habits in certain rocks and not in others.

Several independent factors may be involved and oversimplification may obscure rather than clarify the problem. The accumulation of observations on zircon in rocks may be used to examine the above suggestions, although no clear solution can as yet be given.

Rapid cooling can probably be ruled out relatively easily as a factor in producing highly elongated zircons; leastways no regular pattern can be found in the elongations of zircons of volcanic, hypabyssal, or plutonic rocks, or in samples from large or from small intrusives. Suggestions of undercooling (Claus) or low viscosity (Hoppe) seem somewhat contradictory, and again the geologic evidence does not support these suggestions in a consistent manner. However, such conditions may have obtained early in the consolidation of the magma, and may have changed completely at a later stage, leaving no trace of their earlier operation, except in the habit of the zircons. It seems natural to expect low viscosity to result in more elongated crystals, but the viscosity may have increased subsequently (e.g., by dissipation of fugitive constituents), during the crystallization of the main constituent minerals. The writer has encountered granite pegmatites with long-prismatic, normally elongated, stubby, or rounded zircons. Following the same line of thought, it is noteworthy that long-prismatic zircons are equally unusual in alkaline rocks as in calc-alkaline rocks, and particularly that the prismatic habit is supplanted by a bipyramidal habit in many peralkaline rocks.

Wyatt's suggestion involves geologic environment rather than specific conditions, but it is also not generally applicable. Elongated zircons may be found in contaminated granites, but such rocks do not invariably have elongated zircons. It is also not true that rocks with long-prismatic zircons are invariably contaminated in the sense used by Wyatt.

From existing data the writer is not able to find a simple solution to this problem. In southern Africa there are only a few granites with much elongated zircons. The Cape granite in the extreme south, with doubly terminated crystals, is emplaced in slightly metamorphosed but apparently very ancient sediments. The Salem and Spitzkoppe granites are in the west. Insufficient specimens of the Salem granite have been examined to ensure that the highly elongated habit is characteristic of that granite. Both these western granites have zircons which are badly terminated; apparently a characteristic also of those basaltic and associated rocks which have long-prismatic zircons. In the U. S., granites with highly elongated zircons seem to be more common in the Appalachians and Rocky Mountains, at least several sediments and metasediments examined in this laboratory contain long-prismatic zircons. However, the only large igneous body with such crystals found so far is the Pend Oreille pluton. This probably reflects the writer's limited experience of American granites. The only effusive rock with long-prismatic zircons encountered so far comes from Japan (table 2). Quite naturally these observations raise the question whether highly elongated zircons mark particular phases or cycles of igneous activity. Read (1955, p. 424-426) has discussed the problem of the time span of any one Granite Series, from which it is clear that two or more Granite Series may overlap in time and in place (see also Backlund, 1943, p. 136-137). The question arises whether possibly

granites with long-prismatic zircons represent the early intrusive members of each Series.

Another avenue must be explored and is apparent from similarities in habit of zircons (long-prismatic, badly terminated) in some basaltic rocks, associated differentiates (igneous granophyres and albitites), and a few granites. A significant first step might be to compare zircons of andesites of Pacific islands remote from continental portions of the Earth's crust with those of continental andesites. Such a comparison may contribute to the problem of the "andesite line" (Marshall, 1912, p. 28).

## CONCLUSIONS

The main conclusions of this paper are:

1. Zircon studies of igneous rocks may yield valuable guides to the petrogenesis of the rocks.

2. Their use in attempts to correlate igneous rocks is more doubtful and can be accepted only if there is other, independent evidence for correlation.

3. Quantitative classifications of zircon concentrates are at all times to be preferred to qualitative classifications. Measurements of crystal size seem particularly helpful.

4. In basaltic rocks the crystallization range of zircon is apparently of the order of 900°-1000°C. Zircon therefore crystallized after the bulk of the main constituent minerals. Zirconium may be present in the lattice of early, magnesian pyroxenes.

5. In alkaline rocks, zircon may be of early, or of late formation, or in peralkaline rocks the mineral may be supplanted by zircono-silicates. Apparently bipyramidal habits become common in zircons of more extreme alkaline rocks.

6. In calc-alkaline rocks zircons are of early crystallization. Most intrusives have a majority of euhedral zircons, but in late differentiates or in extrusives, corroded and rounded crystals may predominate.

7. The size and predominant characters of zircons are apparently invariant or closely similar throughout a body of magmatic granite, despite some petrographic variation in the main constituents of the rocks. However, extreme differentiates may have somewhat different zircons which, nonetheless, may be related to those of the parent rocks. If no relations can be found between the zircon concentrates, it may indicate that the intrusive is composite.

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Department of Geology
Columbia University
New York, N. Y.

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# Rb/Sr AGE, ELEMENTAL AND ISOTOPIC ABUNDANCE STUDIES OF STONY METEORITES

LEONARD F. HERZOG and WILLIAM H. PINSON, Jr.

ABSTRACT. The concentrations of Rb and Sr in two chondritic meteorites have been determined by the stable isotope dilution method, and Sr isotope abundances of the chondrites and an achondrite with a large $\frac{Sr}{Rb}$ ratio investigated. Age and original $^{87}Sr$ relative abundance relationships for the chondrites and the Earth are given.

Homestead chondrite Sr shows a 5% enrichment in the radiogenic isotope $^{87}Sr$, compared to a terrestrial standard with isotope abundances nearly identical to those of recent oceanic Sr, while the abundance ratios of the other isotopes, 84, 86 and 88, in meteorite and standard are very closely identical. The precision of these measurements (as relative standard deviation) is $\pm$ 0.4%. Forest City chondrite Sr appears to be essentially identical in isotope composition. Pasamonte achondrite Sr is identical in 84, 86, and 88 ratios, but depleted by 1.5-3.0% in $^{87}Sr$.

The Rb and Sr concentrations measured for the meteorites, with the metallic phase extracted prior to analysis, are as follows: Homestead, Rb = 4.0 $\pm$ 0.4 ppm by weight; Sr = 11.9 $\pm$ 0.5, 10.7% metal extracted. Forest City, Rb = 4.3 $\pm$ 0.3; Sr = 12.1 $\pm$ 0.5, 19% metal extracted. (Total meteorite abundances are given in the text.) The Rb values are lower than those previously accepted.

Recent determinations and estimates of chondrite ages by the U/Pb, K/A and other methods yield values of (4.2-5.2) x $10^9$ years. The abundance of $^{87}Sr$ in Homestead Sr 4.7 x $10^9$ years ago was 0.0682 $\pm$ 0.0005, if the half life of $^{87}Rb$ is 61.3 x $10^9$ years, or 0.0671 $\pm$ 0.0005 if this half life is 50 x $10^9$ years. Further, our previous determinations of Sr isotope abundances in ancient terrestrial minerals with very high Sr/Rb ratios indicate an $^{87}Sr$ abundance of roughly 0.0675 $\pm$ 0.0010 for bulk terrestrial Sr 4.7 x $10^9$ years ago, and the $^{87}Rb$ half life uncertainty does not enter into this extrapolation.

Hence, meteorites and Earth appear to have had identical Sr isotope compositions, including an "original" $^{87}Sr$ concentration ($^{87}Sr_0$) of 0.0683 $\pm$ 0.0010 approximately 4.7 x $10^9$ years ago. This evidence admits the possibility of a contemporaneous origin of these chondrites and Earth about 4.7 billion years ago.

## INTRODUCTION

In a previous paper (Herzog and others, 1954) we reported preliminary analytical work on the Homestead meteorite. A significant enrichment of $^{87}Sr$ had been found, and from optical spectrographic analyses the Sr/Rb ratio was believed to be known to a precision of $\pm$ 30%. However, the accuracy of the optical spectrographic data, especially the Rb content of the meteorite, was in doubt.

Isotope dilution analyses for Rb and Sr have now been made in duplicate for the Homestead sample. In addition, the isotopic composition of this meteorite's Sr has been more accurately determined by another analysis, using refined techniques (Herzog and Pinson, 1955b).

To calculate the age of a meteorite, it is necessary to know its $^{87}Sr$ abundance when it formed. We hoped to obtain this information indirectly by measuring the Sr isotope abundances in a meteorite with a Sr/Rb ratio sufficiently high (>100) that $^{87}Rb$ decay-produced $^{87}Sr$ would produce only a negligible increase in total meteorite $^{87}Sr$ abundance in several billion ($10^9$) years. Published analyses of the achondritic Pasamonte meteorite (Urey and Craig, 1953) indicated that it had a Ca/K ratio of 170, and hence that its Sr/Rb ratio should be greater than 100. We obtained a very small sample of Pasamonte from the National Museum in Washington in 1954 through the kindness of Mr. E. P. Henderson. The Sr from 0.3 gm of this material was

separated, and its isotopic composition was analyzed. The analysis for $^{87}Sr$ was unsuccessful because the small $^{87}Sr$ signal obtained was swamped by a small amount of contamination $^{87}Rb$ (the ionization efficiency of the surface ionization source used in this work is more than 1000 times greater for Rb than for Sr), although analysis for the other isotopes was successful. The remaining gram of this material was set aside pending improvements in technique which would warrant its use. Since in the interim a technique for more complete separation of traces of Rb from Sr samples, and an increase of at least a factor of 50 in instrumental Sr sensitivity have been achieved (Herzog, Pinson, and others, 1955, p. 18, 22), analysis of a new Pasamonte Sr sample has been started. This analysis indicates that Pasamonte Sr is indeed lower in $^{87}Sr$ content than standard Sr by at least 1.5 percent.

When the first Pasamonte analysis failed, it was decided to analyze the Forest City chondrite. A sample was available, and previous spectrographic analyses (Pinson, 1951) indicated that it had a Sr/Rb ratio double that of Homestead, which, if true, would permit moderately precise solution for original meteoritic $^{87}Sr$ and age by extrapolating the $^{87}Sr$ abundances in the two meteorites backwards in time until they were equal. However, isotope dilution analysis showed that the Sr and Rb contents of the meteorites were very similar, and hence that the reported differences were due to experimental error, and this pair of meteorites was unsuited for the determination of $^{87}Sr_0$. Indeed, the isotope dilution run data indicate that $^{87}Sr/Sr$ in Forest City is identical to Homestead $^{87}Sr/Sr$. (A separate isotopic analysis run on unspiked Forest City Sr has not yet been made.) Thus, at present, the predicted original $^{87}Sr$ abundance has not been observed; however, sufficient information has been gathered to allow a well founded prediction of this value for both terrestrial and meteoritic matter: very probably, $^{87}Sr_0 = 0.0683 \pm 0.0010$, and this range includes a 20% uncertainty in the $^{87}Rb$ half life. Also, the Rb and Sr and isotope analyses made are of some general interest; we have decided therefore to present the information we have at present, even though the age portion of the work is incomplete.

## ANALYTICAL PROCEDURES

Descriptions of the meteorites analyzed are contained in Prior's (1953, p. 124, 157) recent catalogue. For these analyses, the metal phase was extracted magnetically. Optical spectrographic analysis had shown the metal and sulfide phases of meteorites to contain negligible Sr and Rb compared to the silicate phase. From the Homestead chondrite, 10.7% metal was extracted, and from Forest City, 19%. The sulfide phase in chondrites averages about 5% by weight; this proportion is fairly constant. Sulfide was not removed because of the difficulty of the separation.

All concentrates for mass spectrometric analysis were prepared by dissolving samples in HF, with the exception of the first Homestead Sr isotope analysis run. With this exception, in all cases small amounts of insoluble residue, less than 1% of sample weight, were left. Optical spectrographic analysis showed these residues to contain negligible Rb and Sr. In the first analysis, the sample was fused with $Na_2CO_3$. A tracer experiment showed

that a considerable ($> 5$ $\mu$gm) amount of Sr contamination had been introduced, necessitating a large correction to the observed $^{87}Sr$ abundance; therefore, in the new analysis, $Na_2CO_3$ fusion was not used. Negligible contamination Sr was introduced, a much larger Sr sample was successfully applied to the filament, there was no Rb interference present, measurements were made on a less sensitive instrument scale, and a much superior analysis was obtained.

*Contamination.*—Stable isotope tracer experiments indicate that less than 0.5 $\mu$gm of Sr contamination are introduced in the processing of one-gram samples by present procedures, and in fact no Sr contamination has been detected. Rb contamination level for our processing of meteorite samples has not been measured directly as yet. However, a contamination level of less than 0.1 $\mu$gm/gm of sample is indicated (as described below) by a similar experiment performed for K contamination (Greenwalt, Herzog, and Pinson, 1955) for a procedure very similar to that used for our Rb analyses. But since the Rb analyses required one additional step (ion exchange column separation), it is possible that the Rb contamination level may have been slightly higher in these experiments.

A 6" radius, 60° sector-field machine with a thermionic source was used for the mass spectrometric work reported. Rb and Sr ions were produced from RbCl, $Rb_2HPO_4$, and SrO on clean or oxidized Ta ribbon supports. Procedures used have been described in detail in previous annual reports of the Nuclear Geophysics Section (Herzog and others, 1954, 1955) of this department.

## Sr and Rb abundances

Table 1 gives the Rb and Sr contents of the combined silicate and sulfide phases of the two chondrites analyzed. Table 2 includes the comparable values for total meteorite.

Table 1

Sr and Rb Contents of Combined Silicate and Sulfide Phases of Two Meteorites, by Isotope Dilution

| Sample | % Metal extracted* | Dates of analyses | Sr ppm | Rb ppm | Sr/Rb |
|---|---|---|---|---|---|
| Homestead I | 10.7 | 15 Oct.-2 Nov. 1954 | 12.3 | 4.4 | 2.8 |
| Homestead II | 10.7 | 20-30 Nov. 1954 | 11.5 | 3.6† | 3.2 |
| Homestead Avg. | 10.7 | — | 11.9 | 4.0 | 3.0 |
| Forest City | 19.0 | 1-15 Apr. 1955 | 12.1 | 4.3** | 2.8 |

* See "analytical procedures" above for discussion of Rb, Sr content distribution among the three meteorite phases.

** Edwards and Urey (1955) have recently measured Rb in Forest City; see table 2 for comparison of values.

† It is not known whether the 20% difference between the first and second Homestead Rb analyses is due to contamination in the first run, or merely indicative of total analysis reproducibility for low level Rb analyses at this time. Much-improved chemical techniques were used for the second analysis, but the mass spectrometer run was subaverage. A third Rb analysis is in progress.

TABLE 2

Comparison of Total Chondrite Strontium and Rubidium Analyses

All analyses expressed as parts per million by weight

| | Rubidium | | | | Strontium | | |
|---|---|---|---|---|---|---|---|
| Meteorite | APK | Rev | EU | HP | P | PAF | HP |
| Homestead | 12.0 | 6 | — | 3.6 | 12 | 18 | 10.6 |
| Forest City | 6. | 3 | 5.8 | 3.5 | 10 | 15 | 9.8 |
| Waconda | 10. | 5 | 4.0 | — | 9 | 11 | — |
| Barratta | 13. | 6 | 6.0 | — | 7 | 9 | — |
| Avg. chondrite | 8.3 | 4.0 | 5.2 | — | — | 11 | — |

APK = Ahrens, Pinson, and Kearns, 1952.
Rev = APK revised, on basis of isotope dilution Rb standardization.
EU = Edwards and Urey, 1955, employing distillation of Rb and flame photometer analysis, ± 25% stated precision.
HP = Herzog and Pinson, present work.
P = Pinson, 1951, thesis; Sr in W-1 diabase = 190 μgm/gm used as standard of comparison.
PAF = Pinson, Ahrens, and Franck, 1953, a revision of P, using 290 μgm/gm for W-1 Sr, and additional analyses.

Avg. Chondrite = Average of 21 analyses for APK and PAF, 3 analyses for EU.

The Rb abundances reported in table 1 are lower than previous analysts have reported for other fragments of the same meteorites, as shown in table 2. Recent isotope dilution experiments (Herzog and Pinson, 1955a, and in press) indicate that all previous M.I.T. Cabot Spectrographic Laboratory Rb analyses, including those of 21 chondrites (Ahrens, Pinson, and Kearns, 1952), are very probably about 2.1 times too high and should be revised. This estimate is based on 8 samples analyzed by both methods. Such revision gives 4.0 ± 0.6 ppm for the Rb content of average chondrite.

The Sr abundances reported are very similar to those found by Pinson (1951), who used 190 ppm for the Sr abundance in the standard diabase, W-1, which was his measurement standard. The values published by Pinson, Ahrens, and Franck are higher because the average of several analyses for Sr in W-1 at various laboratories, 290 ppm, was used to recalculate the measurements. We have recently found 177 ± 7 ppm Sr in W-1 by isotope dilution (Herzog and Pinson, 1955c).

The data presented by Ahrens, Pinson, and Kearns yielded a ratio for K/Rb = 100 (840 ppm K, 8.3 ppm Rb for average chondrite). Diminishing the Rb value found by a factor of 2.1 to make these analyses consistent with the isotope dilution determinations of Rb in identical samples, as discussed above, yields K/Rb = 210. Our isotope dilution determinations of K/Rb for Forest City and Homestead average 265 (this work, and Greenewalt, Herzog, and Pinson, 1955), while the average for the three samples analyzed by Edwards and Urey by optical spectrograph is 180. Thus the true K/Rb ratio

[1] Greenewalt and others (1955) found 19 μgm/gm of contamination K in his recent meteorite processing, indicating about 19/220 ≃ 0.1 μgm/gm of Rb contamination for this procedure, since the K/Rb ratios for laboratory contamination and meteoritic matter are very similar. (See, for example, Pinson, Ahrens, and Franck, 1953, for a discussion of the variation of K/Rb in terrestrial materials.) This determination is further discussed in the section on analytical procedures.

for average chondrite now appears to be about 220, with an estimated uncertainty of ± 25%.[1]

### ISOTOPIC ANALYSES OF METEORITE Sr

The isotopic composition of Homestead meteorite Sr is compared to that of a "normal" terrestrial Sr standard as reported by Nier (1938) and also by Herzog and others (1953), in table 3.

As was noted in the introduction, the isotopic analysis made on December 14, 1954 is believed to be greatly superior in quality to the first analysis, made in February, 1954, because of interim improvements in technique. For this reason, the later analysis alone has been used in the age calculations carried out below.

There is only about a 1% difference between the 86/88 ratio measurements of Homestead and terrestrial standard Sr, and in fact the entire difference may represent experimental error, although in general our reproducibility for Sr samples is rather better than this. The 84/88 ratios are similarly in agreement. However, the 87/88 ratios, ratios of a radiogenic to a non-radiogenic isotope, are different by about 5%. The enrichment in radiogenic strontium in the meteorite is real and far outside the limits of analytical error. Considering the measured Sr/Rb ratio, an extreme antiquity is indicated for the meteorite.

An independent isotopic composition analysis of Forest City Sr has not been made as yet. However, its $^{87}Sr$ content can be closely estimated from the isotope dilution data. If we assume that the 84/88 and 86/88 ratios in Forest City Sr are essentially normal (as they are in Homestead and Pasamonte Sr), the calculated $^{87}Sr$ content of Forest City Sr is (7.365 ± 0.050)%, which is identical, within the stated limits of error, with $^{87}Sr$ in the Homestead meteorite, (7.335 ± 0.030)%.

Pasamonte achondrite Sr is also identical, within the stated limits of error, with our standard Sr in its relative 84, 86, and 88 contents but is depleted in 87 by at least 1%. We have not yet had a completely satisfactory analytical run on this sample, in part because we had available only 0.2-0.5 gram per run.

In the first run, the Rb current was so large that $^{87}Sr$ could not be calculated with useful precision; also, the Sr current was only slightly above the detectability threshold. In the second run, the Rb current was very small, and the Sr current about the same as in the first run, but, in the meantime, instrumental sensitivity had been increased more than 100 fold. However, during part of the run tube pressure was above $1.0 \times 10^{-6}$ mm Hg so that there was some ion beam broadening. As we were most interested in establishing an *upper limit* for Pasamonte $^{87}Sr$, we corrected conservatively for these effects in obtaining the values (e.g., 87/86 max = 0.0703 ± 0.0003) listed in table 3. $^{85}Rb/^{87}Rb$ was assumed to be 2.60, which is the ratio in ordinary rubidium, although "memory" effects from previous isotope dilution runs often cause lower ratios in the accumulated Rb inside the analytical mass spectrometer; also, no pressure correction was made. If, instead, reasonable pressure broadening corrections are made, and the $^{85}Rb/^{87}Rb$ ratios observed

TABLE 3

## Meteorite Isotope Abundances

Mass spectrometric measurement precision, as relative standard deviation, for all measurements is ± 0.4%, except: ± 2.0% for the 1954 Pasamonte ratios reported and all 84 measurements, and ± 0.6% for $^{87}Sr$ in Forest City.

| Run | No. sets | Observed Ratios 87/88 | 86/88 | 84/88 | 87/86 | Relative Abundances 84 | 86 | 87 | 88 |
|---|---|---|---|---|---|---|---|---|---|
| Homestead | | | | | | | | | |
| 9 Feb. 1954 (Contaminated) | 148 | .0875 | .1190 | .0069 | .735 | .0057 | .0981 | .0722 | .8240 |
| 14 Dec. 1954 (Scales changed)* | 50 | .0892 | .1186 | .0069 | .752 | .0057 | .0976 | .0734 | .8233 |
| 14 Dec. 1954 (Scales not changed)* | 92 | .0890 | .1181 | .0069 | .754 | .0057 | .0973 | .0733 | .8237 |
| Average for 14 Dec. analysis | 142 | .0891 | .1183 | .0069 | .753 | .0057 | .0974 | .0733 | .8235 |
| Forest City | | | | | | | | | |
| 1-15 Apr. 1955 (isotope dilution)** | 20 | — | (.1194) | (.0068) | — | — | — | .0736** | — |
| Pasamonte | | | | | | | | | |
| 27-29 Oct. 1954 | 48 | — | .1210 | .0067 | — | — | — | — | — |
| 10-20 Aug. 1955 | 111 | .0842† | .1197 | .00682 | .703† | .00563 | .0989 | .0695† | .8259 |
| Nier's Normal Sr | | .0850 | .1194 | .0068 | .712 | .0056 | .0986 | .0702 | .8256 |

* For some groups of peak sets, all isotopes were recorded at the same sensitivity scale setting of the strip chart recording potentiometer, while for other groups sensitivity was changed in such a way as to make the recorded peak heights of the less abundant isotopes comparable to the trace of the abundant 88 peak.

**Determined incidental to isotope dilution analysis for Sr concentration. $^{87}Sr$ solved for on assumption 84/88 and 86/88 are identical to values for standard Sr ("Nier's Normal Sr").

† Maximum, as small Rb contamination and pressure broadening corrections were made conservatively. Values up to 1.5% smaller are permitted by the uncertainties in these corrections (e.g., $0.703 \geqslant {}^{87}Sr/{}^{86}Sr \geqslant 0.691$).

during the run are used in correcting for $^{87}Rb$, $^{87}Sr$ values up to 1.5% lower (e.g., $87/86 = 0.0691 \pm 0.0003$) result. We believe the true $^{87}Sr$ value for Pasamonte lies within this range, possibly nearer the upper limit. We plan another analysis to determine this important value more exactly.

## PREMISES OF Rb/Sr AGE DETERMINATION

For the calculation of the Rb/Sr age of a meteorite the following quantities must be known:

(1) The Sr and Rb content of the sample.

(2) The fraction of Sr which is radiogenic, hence,

  (a) The present fraction of $^{87}Sr$ in total sample Sr.

  (b) The original fraction of $^{87}Sr$ in total sample Sr.

(3) The present fraction of $^{87}Rb$ in total sample Rb, and the variation of this fraction in past time.

(4) The decay constant of $^{87}Rb$, implicit in (3).

Also, a necessary condition for age determination is that the sample shall have been a closed system in so far as ingress and egress of Rb and Sr is concerned, since the object was formed.

Items (3) and (4) have been previously discussed (Herzog and others, 1954) and will not be repeated here.

The condition that the sample shall have been a closed system is a serious one to be met in *all* radioactivity methods of age determination. This condition is perhaps more favorably satisfied by meteorites than any other rock or mineral samples analyzed. If meteorites have been isolated in space, they have not been subjected to metamorphic processes and to possible leaching by ground or magmatic waters as are terrestrial samples. However, it should be noted that laboratory experience indicates that the alkali metals K, Rb, and Cs are copiously vaporized, in vacuo, at temperatures below red heat. There is some evidence that most meteorites have not undergone such heating since their last crystallization. An example of this evidence is the existence of Widmanstätten figures in metal meteorites. However, perhaps the strongest evidence is the near constancy of the alkali trace element content of chondrites, which has been investigated by optical spectrograph (Ahrens, Pinson, and Kearns, 1952; Pinson, Ahrens, and Franck, 1953; Edwards and Urey, 1955). Had some chondrites undergone heating (as for example by passing close to the Sun), these meteorites would be depleted in volatile elements such as K and Rb. Numerous analyses have failed to find any anomalously alkali-low chondrites. The Homestead and the Forest City chondrites are normal in their alkali contents, and it is tentatively concluded that these two chondrites have not been heated since their formation.

The present fraction of $^{87}Sr$ in total sample Sr, item (2a), has been determined. However the original fraction of $^{87}Sr$, item (2b), cannot be directly determined, but must be estimated by methods such as those discussed below. It should be emphasized that this difficulty is inherent in most radioactivity age determination methods. For example, most ages by the U/Pb, Pb/Pb, or Th/Pb methods assume a knowledge of the initial isotopic composition of Pb. The case of uraninite U/Pb ages, where only negligible

amounts of common Pb are present in the sample, is directly comparable to the case of lepidolite, where often only negligible amounts of common Sr are included in the mineral. In both cases knowledge of daughter element isotope composition at the time of crystallization of the mineral is superfluous.

## AGE CALCULATIONS

For the Homestead meteorite all the quantities necessary for age determination are known except the initial isotopic composition of the Sr, and this knowledge may not be obtained directly. However, the near identity of the non-radiogenic isotope ratios 86/88 and 84/88 in meteorites and terrestrial Sr may be used as an argument that initially terrestrial and meteorite Sr had the same isotopic composition.

Table 4 gives two "ages" calculated on two assumptions as to the initial Sr isotopic composition of Homestead meteorite. [0.2785 (Nier, 1950) was used for the relative atomic abundance of $^{87}$Rb.] Next, an age of 4.7 x $10^9$ years is postulated for meteorites, and the abundance of $^{87}$Sr at that time in Homestead meteorite Sr is computed on the basis of two possible $^{87}$Rb half lives.

*Discussion.*—1. A "minimum age" of 2.8 x $10^9$ years is obtained if the initial abundance for $^{87}$Sr is assumed to have been 0.0702. This is the relative abundance in the terrestrial reagent Sr standard previously mentioned (Nier, 1938; Herzog and others, 1953). We have been unable to discover the geological source of this "standard Sr"; however, the value 0.0702 is typical for Sr extracted from limestones of Paleozoic age (Herzog and others, 1954).[2] The $^{87}$Sr abundance for a Recent or Pleistocene coquina from the Florida east coast (Herzog and others, 1954) is 0.0705 ± 0.0003.

2. Our analysis (above) indicates that $^{87}$Sr/Sr in Pasamonte achondrite Sr today is less than 0.0695 ± 0.0003, and its Ca/K ratio is so high that, very probably, $^{87}$Sr/Sr in the meteorite has changed very slightly, perhaps 0.0002 ± 0.0002, in 5 × $10^9$ years. If original $^{87}$Sr abundances were identical in achondrite and chondrites (as their 84, 86, and 88 abundances are, apparently, identical), a value in the range 0.0687 ± 0.0008 should be used for $Sr_0$ in calculating the chondrite ages.

We have also found terrestrial $^{87}$Sr abundances as low as 0.0692 ± 0.0005 for ancient calcic plagioclases with Sr/Rb ratios greater than 100. It

TABLE 4

Age and Initial $^{87}$Sr Abundance Relations for the Homestead Meteorite

| | Initial $^{87}$Sr content | Half life of $^{87}$Rb assumed | "Age" in $10^9$ year units |
|---|---|---|---|
| | Assumed | | Calculated |
| 1. | 0.0702 | 61.3 x $10^9$ yrs. | 2.8 ± 0.3 |
| 2. | 0.0692 | " " | 3.7 ± 0.4 |
| | Calculated | | Assumed |
| 3. | 0.0682 ± 0.0005 | " " | 4.70... |
| 4. | 0.0671 ± 0.0005 | 50.0 x $10^9$ yrs. | 4.70... |

[2] But at least some of the samples analyzed may be "recent" exchanged Sr.

seems reasonable to assume that the meteorite had an initial 87 abundance at least as low. Initial 87 abundances of less than 0.0692 lead to ages greater than 3.7 billion years. A half life of 61.3 x $10^9$ years was used in both the preceding calculations.

3. Patterson (1955) has found the ages of several meteorites, including Forest City, to be very close to 4.5 x $10^9$ years. His results appear to us to be the most dependable age measurements made up to the present, especially since the leaching and addition problem that makes terrestrial U/Pb measurements questionable is not present for meteorites. Extreme chondrite antiquity is also indicated by recent K/A age measurements by Wasserburg and others.[3] These recent radioactivity determinations of solar system ages, and estimates based on astronomical data, for the most part fall in the range (4.7 $\pm$ 0.5) x $10^9$ years.

If the Homestead age is 4.7 x $10^9$ years and the $^{87}$Rb half life is 61.3 x $10^9$ years, the original relative 87 abundance of Homestead Sr can be calculated as 0.0682 $\pm$ 0.0005. The value derived, of course, depends on the half life. We have used 61.3 x $10^9$ years heretofore in order to make possible direct comparison of our results with those of the group at the Carnegie Institution of Washington. This value was selected in 1953 as it was strongly indicated as correct by the then most recent investigations of the half life by counting techniques.

4. However, comparison of our recent age measurements and those of Aldrich and his colleagues at the Carnegie Institution (Aldrich, Tilton, and Wetherill, in press) with the most reliable U/Pb ages for the areas investigated shows a rather consistent difference which would vanish if the $^{87}$Rb half life was about 50 x $10^9$ years. A very recent counting determination of the half life, by Geese-Bähnisch and Huster (1954), in which quite elaborate controls and interchecks were used, indicates that the half life may be as low as 43 x $10^9$ years. Actually, as it is necessary to extrapolate the low energy portion of the beta decay spectrum owing to failure of present techniques below 10-20 KeV, all the counting results are subject at present to an uncertainty of at least 10%, regardless of other factors.

Thus, a calculation based on a half life of 50. x $10^9$ years is of some interest, and has been included in the table. The corresponding value for $^{87}Sr_0$ is 0.0671 $\pm$ 0.0005.

### TERRESTRIAL $^{87}$Sr VARIATION

Original $^{87}$Sr values in the range 0.0665-0.0685 are supported by another line of evidence. Wickman (1948) and others predicted a large variation in the $^{87}$Sr content of terrestrial Sr during geologic time on the basis of a then indicated crustal Sr/Rb ratio of about 1, or less, and pointed out that such

[3] Recent analyses by Wasserburg and Hayden (1955), using the K/A decay, support this work, and the K/A results of Thomson and Mayne (1955) and Gerling and Rik (1955) also indicate the great antiquity of at least most chondrites. However, these "argon ages" are at present subject to an uncertainty of at least $\pm$ 20% in the K/A half life (and the A/Ca branching ratio) of the K decay. Hence, the U/Pb ages, in which two decays, of $^{235}$U and $^{238}$U, give the possibility of confirmation of results, appear much more trustworthy at this time.

a variation could be used as a dating method for limestones, calcic plagioclases, and other high Sr/Rb ratio minerals. Although many samples of different ages have been analyzed to test this possibility (Herzog and others, 1953, 1954), the expected depletions in $^{87}Sr$ have not been found. The lowest abundance observed for a calcic plagioclase of presumed age greater than $1.5 \times 10^9$ years, as mentioned above, was $0.0692 \pm 0.0005$. On the basis of these studies we now believe that in $4.7 \times 10^9$ years the relative abundance of $^{87}Sr$ in total terrestrial Sr has varied only between the limits of $0.0675 \pm 0.0010$ and the present $0.0705 \pm 0.0003$. Our recent finding that one laboratory's Rb determinations used in calculations such as those of Wickman were uniformly too high by a factor of about 2.1 (Herzog and Pinson, 1955) offers at least a partial explanation for the discordance of the predicted and observed variations.

## SUMMARY AND CONCLUSIONS

These investigations indicate that at some time in the immediate vicinity of $4.7 \times 10^9$ years ago, silicate meteorite Sr and terrestrial Sr had identical relative abundances of the radiogenic isotope $^{87}Sr$ of $0.0683 \pm 0.0010$; further, the ratios of the other, not appreciably radiogenic isotopes, 84, 86, and 88, were and are now identical, within the limits of experimental error, $\pm 0.5\%$ standard deviation. This evidence admits the possibility that Earth and meteorites may have formed contemporaneously about $4.7 \times 10^9$ years ago, and conforms with the U/Pb and K/A evidence recently obtained by others.

These statements rest on the following data:

1. The silicate-sulfide phases of the Homestead and Forest City chondrites are closely similar—identical, within the limits of error of the present measurements—in Sr and Rb concentration ($12.0 \pm 0.5$ and $4.0 \pm 0.4$ p.p.m. by weight) and ratio, and in Sr isotope composition, both having $^{87}Sr/Sr$ today $= (7.35 \pm 0.05)\%$. If the $^{87}Rb$ half life is $(55 \pm 6) \times 10^9$ years, $^{87}Sr/Sr$ concentrations $4.7 \times 10^9$ years ago in these meteorites were $0.0677 \pm 0.0010$.

2. $^{87}Sr/Sr$ in Pasamonte achondrite material today $= (6.89 \pm 0.08)\%$. Since the Ca/K ratio in this meteorite is, reportedly, 170, this value has in all probability not increased more than $(0.02 \pm 0.02)\%$ in $4.7 \times 10^9$ years and was then $(6.87 \pm 0.08)\%$; this value is insensitive to even large errors in the assumed $^{87}Rb$ half life.

3. Studies of ancient terrestrial minerals with very large Sr/Rb ratios ($>100$) indicate that terrestrial $^{87}Sr/Sr$ was in the range $(6.75 \pm 0.10)\%$, $4.7 \times 10^9$ years ago. This result is independent of the $^{87}Rb$ half life as the sample ages were estimated by other methods.

Unfortunately, the original $^{87}Sr$ data so far obtained are not sufficiently precise to make possible a decision as to the true $^{87}Rb$ half life.

The average Sr content of chondrites, our analysis indicates, is probably $10 \pm 2$ ppm by weight, in agreement with the most recent optical spectrographic analyses (Pinson, 1951; Pinson, Ahrens, and Franck, 1953). How-

ever, chondrites probably average only 4.0 ± 0.6 ppm Rb instead of the 8.3 ppm previously indicated (Ahrens, Pinson, and Kearns, 1952). Generalization from two chondrite analyses is justified because of the demonstrated uniformity of composition of the silicate-sulfide phases of chondrites (Pinson, 1951, et. seq.).

The corrected Rb abundances and verified K analyses for these meteorites indicate, in addition, a K/Rb ratio of 220 ± 50 for average chondrite matter.

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Department of Geology and Geophysics
Massachusetts Institute of Technology
Cambridge, Massachusetts

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# THE BRUCITE-PERICLASE EQUILIBRIUM*

GEORGE C. KENNEDY

ABSTRACT. The equilibrium relations between brucite and periclase + water, $MgO.H_2O = MgO + H_2O$, have been determined to 1400 bars and 640°C. by measuring with a precise Heise bourdon tube gage the water vapor pressure generated on heating brucite. The calculations of G. J. F. MacDonald are confirmed.

This method of determining equilibrium relations capitalizes on the rapid reaction rate in the system and avoids the difficulties of the quenching method where rapid rehydration takes place as the sample is cooled. Changes in surface energy due to changing grain size during the course of an experiment seems to be a major source of discrepancy between curves obtained by hydrating periclase and those obtained by dehydrating brucite.

## INTRODUCTION

The equilibrium between brucite and periclase has been examined in three recent investigations (Bowen and Tuttle, 1949; Roy, Roy and Osborn, 1953; and MacDonald, 1955).

The pressures and temperatures of the equilibrium between brucite and periclase have been determined by both Bowen and Tuttle, and Roy, Roy and Osborn using quenching methods. The results of these two investigations are in considerable disagreement. Roy, Roy and Osborn find the equilibrium temperature at a given pressure some 250°-300°C. lower than the temperature determined by Bowen and Tuttle.

The problem has been approached from the standpoint of thermodynamic theory by MacDonald (1955). Using graphical integration, he evaluated the Gibbs free energy of water at high temperatures and pressures from the recorded P-V-T relations in water (Keenan and Keyes, 1936; Kennedy, 1950). Published values for heat of solution, entropy, and heat capacity of brucite and periclase were used to evaluate the difference in Gibbs free energy of brucite and periclase at various temperatures. Appropriate water pressures were then selected at various temperatures to satisfy the condition of equilibrium that the Gibbs free energy of the reaction be zero.

Recognizing that the disparities in experimental results are partly due to differences in the grain size of the reactants, MacDonald computed two equilibrium curves, reproduced in figure 1 of this paper. Curve A of figure 1 corresponds to the equilibrium between coarse well crystallized brucite and fine-grained periclase, and curve B corresponds to the opposite case of fine-grained poorly crystallized brucite with coarse well crystallized periclase. The equilibrium curve between brucite and periclase in a geological environment, where adequate time is generally available for both phases to coarsen, should presumably lie somewhere between the curves A and B.

The position of the two curves is affected by considerable uncertainty, in addition to that of grain size. An uncertainty of some ±50°C., owing to uncertainties in the P-V-T relations of water and the Gibbs free energy values derived from them, is estimated by MacDonald. Thus the position of the curve as determined by Roy, Roy and Osborn (fig. 1) barely lies within this estimated limit, being almost exactly 50°C. above MacDonald's curve A, and the curve of Bowen and Tuttle (fig. 1) is far above it. An accurate de-

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The Institute of Geophysics
University of California, Los Angeles 24, California

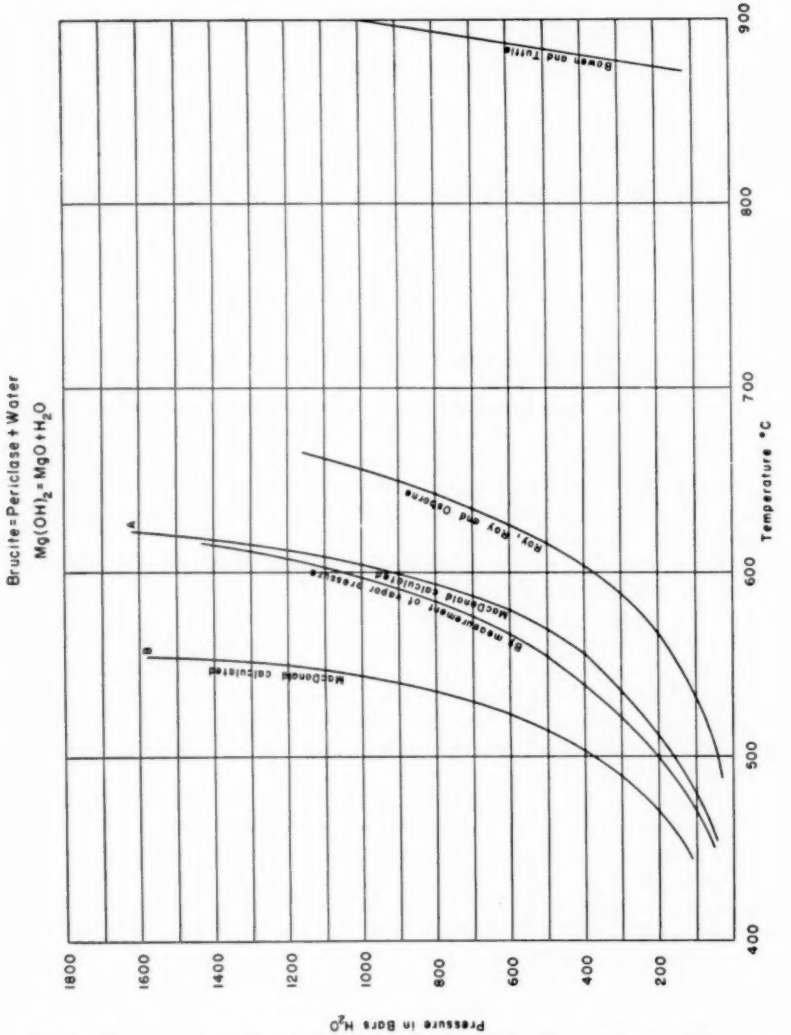


Fig. 1. Summary of results of various workers on the brucite-periclase equilibrium.

termination of the equilibrium curve between brucite and periclase would aid in estimating the inaccuracies of a portion of the existing tables of water properties and in evaluating the uncertainties in the tables of Gibbs free energy prepared by MacDonald.

## PRESENT WORK

One of the major difficulties encountered in previous experimental investigation of the brucite-periclase reaction was that of rate of attainment of

equilibrium. Periclase, largely or in part, hydrates to brucite on quenching in the presence of water. Such rapid hydration and dehydration makes the use of the hydrothermal quenching method for investigations of phase boundaries in this system extremely difficult. For example, Roy, Roy and Osborn (p. 345) found it necessary to assume that periclase is the stable phase at a pressure and temperature where quenched products contain more than 20 to 30 percent periclase.

To avoid the difficulties of quenching, I have attempted to measure directly the vapor pressures at various temperatures involved in the reaction $MgO.H_2O = MgO + H_2O$, and to interpret the vapor pressure data in terms of brucite-periclase relations.

A 200-cc bomb of Inconel X[1] alloy of conventional design was connected by means of a length of capillary tubing to a precise 1400-bar Heise bourdon tube pressure gage, which was calibrated against a deadweight piston gage both before and after the present experiments. To introduce or remove water, a needle valve was seated in the capillary between the bomb and the pressure gage.

The bomb was heated in an electrical resistance furnace. Temperature was regulated by means of a phase-shifting thyrotron bridge circuit.

Temperature was measured by use of calibrated thermocouples. A length of stainless steel tubing of 5/16″ o.d. and 1/8″ i.d. was welded shut at one end, inserted to almost the exact center of the bomb, and secured by means of a pressure-tight seal in the end of the bomb. This served as a thermocouple well and reduced the uncertainty of bomb temperature to no more than 1°C.

## EXPERIMENTAL RESULTS

Approximately 200 grams of Baker's c.p. MgO light powder with barely sufficient distilled water to make a stiff paste was packed into the bomb. The bomb was then sealed and brought to approximately 400°C. Distilled water was then pumped in to bring the pressure to approximately 1000 bars. Pressure and temperature were maintained for a few days, by which time most of the MgO was presumed to have hydrated to brucite. The pressure was then dropped to a low value by bleeding steam from the bomb, and pressure and temperature recorded. The temperature was then raised by increments of a few degrees and a series of observed pressures recorded. A 24-hour period was allowed at each temperature for equilibrium. The vapor pressures for a number of different temperatures were thus determined.

A typical series of pressure versus temperature readings is shown in figure 2. Here the first observation was at 406°C. and 205 bars pressure. As the temperature of the bomb was increased, the pressure increased lineally. Steam table data indicate that the slope of the plot of pressure versus temperature here corresponds to a specific volume of approximately 10 for the steam contained in the bomb. At a temperature of approximately 530°C. and a pressure of 310 bars, an abrupt change in the slope of the plot of pres-

[1] Inconel X alloy proved to be rather unsatisfactory in this particular application. Many radial cracks from the bore of the bomb outward eventually caused failure of the bomb and ended this group of experiments. Dr. George Morey reports similar experience with Inconel X alloy.

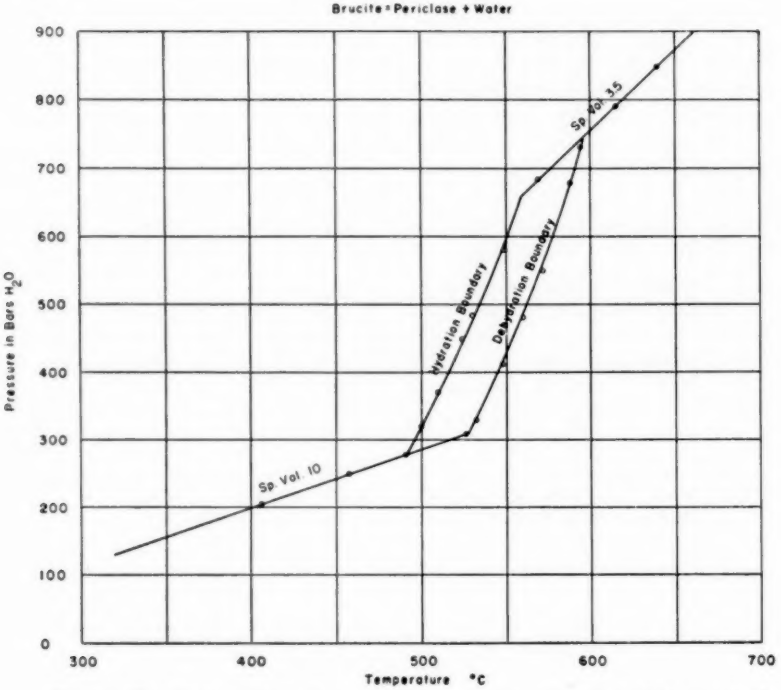


Fig. 2. Plot of observations of pressure versus temperature for a single run in the system MgO—$H_2O$.

sure versus temperature took place. Here the pressure rose rapidly for slight temperature changes owing to the dehydration of brucite and addition of the water to the vapor phase in the system. A second abrupt change in the slope of the pressure-temperature plot took place at 750 bars and 596°C. All the brucite in the bomb had been converted to periclase and pressure rose solely owing to change in temperature of the enclosed steam. The slope of the plot here corresponds to a specific volume for steam of approximately 3.5 and gives a measure of the amount of brucite converted to periclase.

The system was then slowly cooled and the periclase rehydrated to brucite. It is to be noted that the rehydration boundary, determined by cooling, lies some 25 degrees lower in temperature than the curve determined by heating. This difference is probably due to changes in both reaction rate and grain size in the system.

Only 24 hours' waiting time was allowed for each reading of pressure and temperature. Pressure first adjusts itself rapidly as a new temperature is reached, but equilibrium has by no means been reached at the end of 24 hours. Even with waiting times of as much as a week, however, the pressures of hydration and dehydration will not be the same in an experimental system

of this sort because of the difference in surface energy resulting from gross changes in grain size as the reaction proceeds. MacDonald has discussed the effect of grain size on this equilibrium at considerable length. For example, in a dehydration run lasting for a week, the brucite is coarse, as it has been aged in the bomb many days at high temperature and pressure; thus the dehydration boundary probably represents fairly closely the equilibrium between

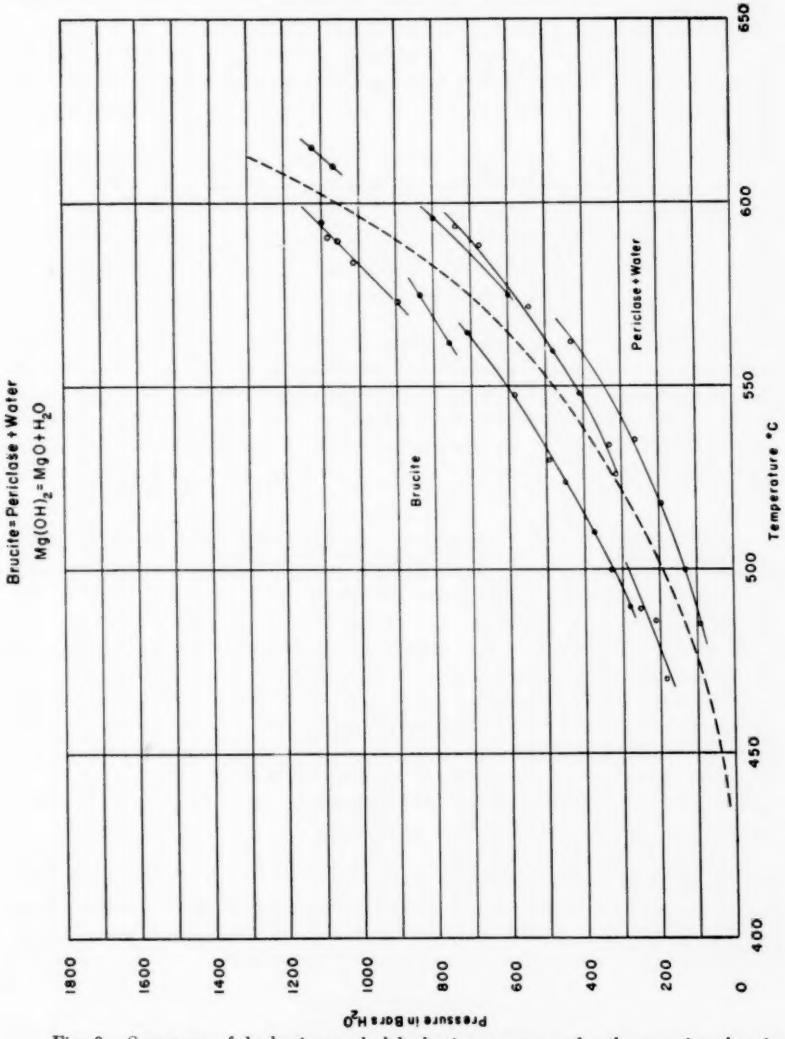


Fig. 3. Summary of hydration and dehydration pressures for the reaction, brucite equals periclase plus water.

moderately coarse brucite and fine-grained periclase produced by the rapid breakdown of the brucite. The converse is true of the rehydration curve. Here, it is the periclase which has had time to age, and the instantaneous product of hydration is fine-grained brucite. In a geological environment, both phases have had sufficient time to be well crystallized and therefore the equilibrium curve presumably lies somewhere between the hydration and dehydration curves as presented here. This mean curve is plotted in dashed lines in figure 3 and is also plotted in figure 1. Giauque (1949) has also recently discussed the effect of grain size on the brucite = periclase + water equilibrium and has emphasized the variation in equilibrium water pressure for the reaction with material of differing grain size and consequently differing surface energy.

As can be noted from figure 2 only a portion of the hydration boundary can be obtained from a single set of readings. Consequently, a series of measurements was made starting with differing initial water pressures in the bomb, and the region from 100 bars to 1400 bars was explored. These sets of readings are plotted in figure 3. Both the groups of hydration and dehydration curves are markedly eneschelon. This is perhaps most easily explained by assuming that the first material in the bomb to react is the finest-grained material and, as the reaction proceeds, successively coarser material reacts with each increment of temperature. Thus the individual sets of results show the effect of changing grain size during the course of the reaction. All curves to the right of the dashed line in figure 3 are hydration curves determined by heating, and those to the left are dehydration curves determined by cooling experiments.

## CONCLUSION

The equilibrium reaction, periclase equals brucite plus water, as interpreted from vapor pressure measurements, lies at pressures and temperatures well within the limits of the curves calculated by MacDonald (1955). The present investigation confirms his calculations and suggestions in a most striking way. MacDonald's free energy values for water are confirmed over the pressure-temperature interval covered by the investigations reported here and, indeed, may have somewhat less than the 5 percent uncertainty estimated by MacDonald. MacDonald's computed curve and the experimental curve agree much better than a 5 percent uncertainty in water values would predict. However, limitations in accuracy of the thermochemical data for periclase and brucite, coupled with the problem of surface energy of material of different grain size, make such claims rather tenuous.

The technique of direct measurement of vapor pressures for determination of hydration boundaries as used in this investigation has certain advantages over the hydrothermal quenching method in those systems where reaction rates are rapid. It is suggested that equilibria between many of the zeolites and anhydrous phases might well be investigated by this method.

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The Institute of Geophysics
University of California
Los Angeles, California

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# RELATIVE AGES OF EASTERN MASSACHUSETTS GRANITES BY TOTAL LEAD RATIOS IN ZIRCON

G. R. WEBBER, P. M. HURLEY, and H. W. FAIRBAIRN

ABSTRACT. The relative lead content of a number of accessory zircon samples separated from eastern Massachusetts granites was determined spectrographically. Selected samples, analyzed for absolute lead content by C. L. Waring of the U. S. Geological Survey, provided a calibration for the remainder. Contents of uranium and thorium were determined by scintillation spectrometer, and the values for total alpha activity calculated from these were checked by total alpha count. The average ratio of thorium to uranium was such that 85% of the radiogenic lead was derived from uranium.

If Waring's calibration values are correct, the lead ratios show two principal ages for the granites as follows:

*260 MY*: Localities near Peabody, Rockport, and Cape Ann; north of North Attleboro; north end of Whitinsville; near Fitchburg.

*355 MY*: Localities north-east of Milford and east of Wrentham.

From the geological relationships it is probable that the granites north and south of Boston known as the Quincy type, as well as part of the area mapped as Dedham granodiorite, and some of the granites extending southward into Connecticut, are all approximately 260 MY. At least one area of granite mapped as Dedham granodiorite was intruded earlier, at 350 MY.

## INTRODUCTION

This investigation has employed the method originated by E. S. Larsen, Jr. and associates of the U. S. Geological Survey (Larsen, Keevil, and Harrison, 1952; Larsen, Waring, and Berman, 1953) for the determination of the age of granite by measurement of the total lead in the accessory zircon by optical spectrograph, and the rate of lead production by alpha count. The zircon was obtained from the granite by use of heavy liquids and magnetic separation, with the modified mechanical procedures described by Fairbairn (1955).

The samples of granite, from 50 to 100 lbs., were collected from a number of quarries and roadside outcrops in eastern Massachusetts. Details of their location are given in table 1. The classification of the Massachusetts granites, given by Emerson (1917), is as follows:

| | |
|---|---|
| Fitchburg granite | Late Carboniferous or Post Carboniferous |
| Quincy granite | Early Carboniferous |
| Milford granite | Devonian ? |
| Dedham granodiorite | Devonian ? |
| Northbridge granite gneiss | Archean ? |

Unfortunately there is a notable lack of fossils in sediments associated with Massachusetts granites. Cambrian fossiliferous strata are found near Quincy (about 10 miles southeast of central Boston) and at Hoppin Hill (about 30 miles southwest of central Boston). At Quincy, the Middle Cambrian Braintree slate is intruded by Quincy granite, a distinctive rock similar petrographically to the granites at Peabody and Cape Ann and correlated with them by field workers. From this evidence it is probable that the Cape Ann and Peabody rocks are post-Middle-Cambrian.

The relationship of the Dedham granodiorite to the Cambrian is more controversial. Rock which has been mapped as Dedham varies considerably petrographically, and it is not unlikely that very different intrusives are included in the classification. At Hoppin Hill, near the Massachusetts-Rhode Island border, the relationship between Hoppin Hill slate (Lower Cambrian) and adjacent granite (classified as Dedham) has been a subject of considerable discussion. Warren and Powers (1914) contended that the granite is younger than the sediments. For a summary of the problem and additional references, see Dowse (1950), who concludes that the granite is older than the sediments and therefore Precambrian in age. Quincy granite in Rhode Island is overlain by basal strata of the Carboniferous Narragansett Basin (Emerson, 1917, p. 188).

TABLE 1
Sample Locations

| Sample No. | Rock | Quarry | Locality |
|---|---|---|---|
| 3004 | Hornblende-augite granite* | Linehan | 3 miles WSW of Peabody |
| 3005 | Hornblende granite | Flat Ledge | 0.5 mile NNW of Rockport |
| 3006 | Hornblende granite | Blood Ledge | 2 miles WNW of Rockport |
| 3011 | Mica diorite | Leavitt | 2 miles W of Leominster, near Fitchburg |
| 3012 | Biotite granite | Norcross | 2 miles NE of Milford |
| 3013 | Biotite granite gneiss | Blanchard | 1.5 miles WNW of Uxbridge, near Whitinsville |
| 3014 | Hornblende granite | Curry | 2.5 miles ESE of Wrentham |
| 3105 | Granite | (Outcrop) | 1.7 miles E of Wrentham |
| 3106 | Biotite granite | West | 1.7 miles NNE of Milford |
| 3107 | Granite gneiss | (Outcrop) | North end of Whitinsville |
| 3108 | Muscovite-biotite granite gneiss | Fletcher | 1.2 mile NW of West Chelmsford Station |
| 3051 | Granodiorite | (Outcrop) | 3 miles N of North Attleboro |
| 3052 | Granodiorite | (Outcrop) | 8.2 miles N of North Attleboro |

* The rocks in most of these localities have been described by Dale (1923).

In areas where Quincy-type granite and Dedham-type granite occur it has been reported that the Quincy is intruded into the Dedham (Emerson, 1917, p. 187-188). In Rhode Island, Quincy granite is intrusive into Milford granite. Emerson states that the Milford granite is intrusive into the Northbridge granite gneiss (p. 155).

The mica diorite from the Leavitt Quarry is on the eastern border of an area mapped by Emerson as Fitchburg granite. The Fitchburg pluton has been tentatively assigned to late Devonian by M. P. Billings (Billings, Rodgers, and Thompson, 1952).

The Quincy granite has been correlated with the White Mountain magma series of New Hampshire by some writers (Williams and Billings, 1938) on

the basis of its alkaline nature. The White Mountain magma series has been dated as probably Mississippian by Billings. Age determinations of the Conway granite of the White Mountain magma series made by Larsen, Gottfried, Waring and others are tabulated by Faul (1954, p. 267). They range from 201 to 255 million years (average 235 MY).

## EXPERIMENTAL PROCEDURES

*Preparation of zircon.*—The granite samples were crushed and ground, and 15 to 30 lbs. of material between the sizes −60 and +200 mesh were obtained from each sample.

Magnetite and tramp iron were removed by permanent magnets and a transverse belt arranged above a thin, moving stream of the sized sample. Magnetite will normally clog up any device used for the magnetic separation of the essential constituents of the rock. Biotite and other dark minerals were removed in a Carpco magnetic separator, leaving the zircon with the light-colored minerals for separation by heavy liquids. Acetylene tetrabromide, methylene iodide and Clerici solution were then used to separate zircon and other heavy accessory minerals. A Frantz magnetic separator was used to separate the zircon from sphene, monazite, and other constituents of higher magnetic susceptibility. Pyrite and other sulphides were dissolved by treating the final sample in hot nitric acid. Remaining impurities were hand-picked from the zircon sample.

The zircon concentrate was then separated into different fractions according to its weak magnetic properties, since it had been found that generally the more magnetic zircon had a higher content of uranium, along with other impurities. The purpose of this fractionation on the basis of magnetic susceptibility, and uranium content, was to test the constancy of age ratios on the same original zircon sample, despite differences in radioactivity and lead content. The separations were made on the Frantz separator using a full field of 1.4 amperes and varying the inclination of the separator. The fraction that is magnetic at 5 degrees is the most magnetic, and the fraction that is non-magnetic at 2 degrees is the least magnetic. These designations are used to distinguish the different fractions in table 2.

*Measurement of uranium, thorium and alpha activity.*—The uranium and thorium content of the zircon samples was determined by a method described by Hurley (1956), utilizing a scintillation spectrometer. The contribution of the gamma rays from the uranium and thorium series was differentiated by a count of the 238 kev gamma rays from lead 212 in the thorium series. The results are given in table 3. It can be seen that, whereas the decay rate of uranium is roughly three times greater than that of thorium, the production of radiogenic lead in the zircon is dominantly from the uranium series. Thus the age ratios are essentially Pb206/U238, if the assumption is correct that there was essentially no lead in the zircon crystals at the time of their formation. On these small zircon samples the precision of the scintillation spectrometer measurements is not quite good enough for this type of work, but the over-all accuracy of the measurements, after allowing for lack of precision, can be good owing to the possibility of direct comparison with well analyzed

TABLE 2
Lead Analyses

| Sample no. | Magnetic fraction* | Replicate Lead Analyses Pb ppm | | | | | | | Average Pb ppm |
|---|---|---|---|---|---|---|---|---|---|
| 3004A | +5° | 47 | 45 | 48 | 42 | 48 | 49 | | 47±1.5** |
| 3004B | +2°–5° | 23 | 20 | 21 | 21 | 22 | 21 | | 21±0.7 |
| 3004C | –2° | 19 | 16 | 20 | 22 | 19 | 19 | | 19±0.6 |
| 3005A | +5° | 134 | 164 | 125 | | | | | 140±6.5 |
| 3005B | +2°–5° | 82 | 84 | 90 | 86 | 86 | 87 | | 85±2.8 |
| 3005C | –2° | 45 | 71 | | | | | | 58±3.3 |
| 3006A | +2° | 33 | 32 | 30 | 45 | 39 | 44 | | 37±1.2 |
| 3006B | –2° | 28 | 29 | 28 | 27 | | | | 28±1.1 |
| 3011A | –2° | 49 | 47 | 44 | 47 | | | | 47±1.9 |
| 3012A | +2° | 87 | 68 | 74 | | | | | 76±3.5 |
| 3012B | –2° | 64 | 49 | 56 | | | | | 57±2.6 |
| 3013A | +5° | 66 | 74 | 66 | 65 | 89 | 66 | 74 | 71±2.1 |
| 3013B | +2°–5° | 65 | 84 | 70 | 58 | 66 | 67 | | 68±2.2 |
| 3013C | –2° | 71 | 73 | 75 | | | | | 73±3.4 |
| 3014B | –2° | 67 | 72 | 68 | 74 | | | | 70±2.8 |
| 3105A | +5° | 110 | | | | | | | 110±8.8 |
| 3105B | +2°–5° | 89 | 90 | | | | | | 90±5.1 |
| 3105C | –2° | 77 | 82 | 72 | | | | | 77±3.5 |
| 3106A | +5° | 110 | 121 | 120 | | | | | 117±5.4 |
| 3105B | +2°–5° | 120 | 129 | 100 | | | | | 116±5.3 |
| 3106C | –2° | 81 | 90 | 72 | 72 | 94 | | | 82±3.0 |
| 3107A | +5° | 71 | 78 | 77 | | | | | 75±3.4 |
| 3107B | +2°–5° | 76 | 66 | 55 | 66 | 65 | | | 66±2.4 |
| 3107C | –2° | 39 | | | | | | | 39±3.1** |
| 3051 | +2° | 57 | 49 | 59 | | | | | 55±2.5 |
| 3052 | +2° | 68 | 65 | 65 | | | | | 66±3.0 |
| 3108A | –2° | 286 | | | | | | | 286±23 |

* Angle on Frantz separator used in magnetic separation.

** Standard deviation precision error based on replicate lead analyses.

uranium and thorium standards. These analyses may therefore be used to check the absorption factor and efficiency in determinations of the alpha activity by direct alpha counting procedures.

The samples were then measured in an alpha counter for alpha particle emission from a thick source. In calculating the alpha activity in alphas/mg hr. within a sample of material, from the measured alpha emission in alphas/cm² hr. from a thick source of the sample in a counter of known geometry, it is necessary to know both the absorption factor and the lower limit of alpha energy that will be recorded by the alpha counter. A source absorption factor for zircon was calculated to be 0.493 by the method described by Nogami and Hurley (1948). In this calculation it was assumed that all alpha particles emerging from the sample would be counted if they had a residual air range exceeding 0.5 centimeter.

The results of the alpha activity determinations by thick source alpha counting are also shown in table 3, after a constant correction factor of 1.16

TABLE 3
Radioactivity Measurements

| Sample no. | Uranium ppm | Thorium ppm | Activity calculated from U and Th $\alpha$/mg hr. | Measured activity from alpha count $\alpha$/mg hr. | Value used in age calculation $\alpha$/mg hr. |
|---|---|---|---|---|---|
| 3004A | 1210 | 375 | 475 | 445 | 455 ± 34** |
| 3004B | 510 | 205 | 205 | 185 | 190 ± 14 |
| 3004C | 405 | 130 | 160 | 200* | 185 ± 14 |
| 3005A | 2765 | 1890 | 1180 | 1250 | 1225 ± 130 |
| 3005B | 2270 | 1200 | 940 | 975 | 960 ± 67 |
| 3005C | 1320 | 740 | 550 | 570* | 560 ± 40 |
| 3006A | 970 | 550 | 405 | 405 | 405 ± 22 |
| 3006B | 630 | 380 | 265 | 270 | 270 ± 20 |
| 3011A | 1130 | 380 | 450 | 560* | 510 ± 50 |
| 3012A | 1350 | 480 | 540 | 455* | 500 ± 37 |
| 3012B | 955 | 445 | 390 | 390 | 390 ± 23 |
| 3013A | 2040 | 1090 | 850 | 830 | 840 ± 60 |
| 3013B | 1875 | 750 | 755 | 680 | 710 ± 70 |
| 3013C | 650 | 480 | 280 | 310* | 300 ± 22 |
| 3014B | 1325 | 680 | 545 | 450 | 490 ± 37 |
| 3105A | | | | 715* | 715 ± 54 |
| 3105B | | | | 680* | 680 ± 50 |
| 3105C | | | | 515* | 515 ± 38 |
| 3106A | 2400 | 915 | 960 | 955 | 955 ± 57 |
| 3106B | 2080 | 705 | 825 | 820 | 820 ± 54 |
| 3106C | 1425 | 490 | 555 | 605 | 590 ± 39 |
| 3107A | 1640 | 1000 | 690 | 720 | 710 ± 70 |
| 3107B | | | | 615* | 615 ± 60 |
| 3107C | | | | 375* | 375 ± 28 |
| 3051 | 1500 | 390 | 585 | 640 | 615 ± 60 |
| 3052 | 1820 | 900 | 750 | 750 | 750 ± 65 |
| 3108A | | | | 830 | 830 ± 69 |

* Sample composed of whole zircon, crystals, not ground.

** Standard deviation precision error based on replicate alpha counts.

had been applied. This factor was determined by plotting the alpha activity determined by alpha count against the alpha activity calculated from the separate uranium and thorium measurements using the scintillation spectrometer. As mentioned previously, although the precision of the scintillation spectrometer measurements is poor, the absolute accuracy of the method is preferred over the calculated absorption factor and efficiency used in the determination of alpha activity from total alpha counts. This adjustment of 16% is therefore applied as an efficiency correction for the counter. It is assumed that the error stems from the counter missing the alpha particles of lowest energy barely emerging from the sample, rather than from the absorption factor, because approximately this difference has also been found between this particular proportional counter and an ionization chamber that gives graphical records of alpha pulses. Alpha particle standards cannot be

used to determine this efficiency factor unless the standard is a homogeneous "infinitely" thick source.

*Spectrographic measurement of lead.*—In spectrographic analysis the problem of absolute accuracy generally consists of obtaining accurate standards composed of the same substance as the samples to be analyzed. The lead content of zircons of late Paleozoic age is low enough so that precise chemical analyses of the lead in standard samples are difficult to make. The ideal method of analysis would be by isotope dilution using a mass spectrometer, and it is hoped that such standards may become available to spectrographic laboratories working on lead measurements of this kind in the future. Because no standards were available for this work, four samples of zircon covering the range of lead content in most of the samples of interest were sent to the U. S. Geological Survey for analysis. It was felt that until such time as absolute standards measured by mass spectrometer become available the best alternative would be to tie in with the analyses made by C. L. Waring of the U. S. Geological Survey who has developed the techniques and standards used in the lead measurements for the laboratory of E. S. Larsen, Jr. and co-workers.

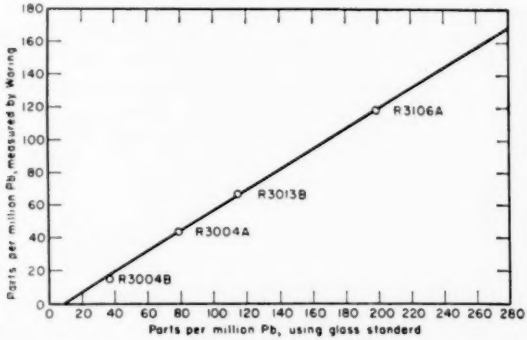


Fig. 1. Calibration of spectrographic analysis of lead in zircon samples.

All the zircon samples, including the four sent to Waring, were first analyzed for relative lead content by the emission spectrograph, using a calibration scale that was found by adding different amounts of a lead-barium glass of known composition to a certain sample of zircon. In figure 1 is shown the relationship between this calibration scale and that used by Waring, as given by the four common analyses. No reason for the failure of the calibration using the standard glass is ventured at this time, but it is mentioned as a warning to those making lead measurements in future by optical spectrograph.

Spectrographic procedures were fairly standard. The zircon was ground to a fine powder in an agate mortar, weighed, and mixed with NaCl so that the resultant mixture contained 80% zircon and 20% NaCl by weight. The sodium chloride was added to improve the arcing qualities of the zircon. The lead line at 4057.820 angstroms was used, in a grating spectrograph (Wads-

worth Mount, 21-ft. instrument) with a dispersion of 2.54 angstroms per millimeter. The lead comes off early, followed after about 35 seconds by an intense line of zirconium which obliterates the lead line's being measured. The arcing was made therefore on the basis of constant time—namely, 30 seconds. All other conditions of arcing and development were maintained as constant as possible.

The results of the lead analyses are given in table 2. Replicate analyses on the same samples give an indication of the precision of the method. As in the case of the activity measurements, it can be seen that there is generally a higher concentration of lead in the more magnetic fractions of each zircon sample.

TABLE 4
Age Results

| Granite type, Emerson (1917) | Locality | Sample no. | Age ratio MY |
|---|---|---|---|
| Quincy | Peabody | 3004A | 260 ± 21 * |
| | | 3004B | 290 ± 23 |
| | | 3004C | 260 ± 21 |
| | Cape Ann | 3005A | 290 ± 33 |
| | | 3005B | 230 ± 18 |
| | | 3005C | 265 ± 25 |
| | Cape Ann | 3006A | 235 ± 15 |
| | | 3006B | 265 ± 22 |
| | Average age for this type | 260 MY | |
| Milford | Milford | 3012A | 385 ± 38 |
| | | 3012B | 365 ± 33 |
| | Milford | 3106A | 310 ± 28 |
| | | 3106B | 360 ± 33 |
| | | 3106C | 355 ± 32 |
| | Average age for this type | 355 MY | |
| Dedham | Wrentham | 3014B | 365 ± 35 |
| | Wrentham | 3105A | 390 ± 43 |
| | | 3105B | 335 ± 31 |
| | | 3105C | 380 ± 33 |
| | Average age for this locality | 365 MY | |
| Dedham | North of N. Attleboro | 3052 | 220 ± 22 |
| | | 3051 | 225 ± 25 |
| Fitchburg | Fitchburg | 3011 | 230 ± 25 |
| Northbridge gneiss | Whitinsville | 3107A | 270 ± 30 |
| | | 3107B | 270 ± 29 |
| | | 3107C | 265 ± 31 |
| Northbridge gneiss | Uxbridge | 3013A | 215 ± 17 |
| | | 3013B | 245 ± 26 |
| | | 3013C | 620 ± 53 |
| Ayer granite | W. Chelmsford | 3108A | 480 ± 51 |

* Standard deviation precision error.

DISCUSSION OF RESULTS

Calculated age ratios are given in table 4. For samples as young as these the simple formula

$$\text{Age} = K(\text{Pb})/A \text{ my}$$

is sufficiently accurate. A is alpha activity in alphas/mg hr., and Pb is the lead content in parts per million. The factor K varies, depending on the ratio of thorium-produced lead to uranium-produced lead in the zircon, between 1985 for all thorium lead to 2670 for all uranium lead. The average Th/U ratio in these zircons is 0.46. Because the distintegration rate of thorium is only 0.32 that of uranium, the ratio of thorium production of lead to uranium production of lead is only 0.15 on the average in these samples. From this the value of K = 2580 was obtained to be used as an average factor for the calculation of the ages.

The principal localities and average age ratios at each point are shown in figure 2. Details are omitted, including the field classifications of the granites.

The samples of the so-called Quincy-type granite show fairly close ages grouped about a mean value of 260 MY. Some of the so-called Dedham granodiorite, north of North Attleboro, Massachusetts, and other granitic rocks to the southwest of Boston near the Connecticut and Rhode Island borders also show this age. A small area in the vicinity of Milford and Wrentham contained granites that were grouped about an age of 355 MY, showing

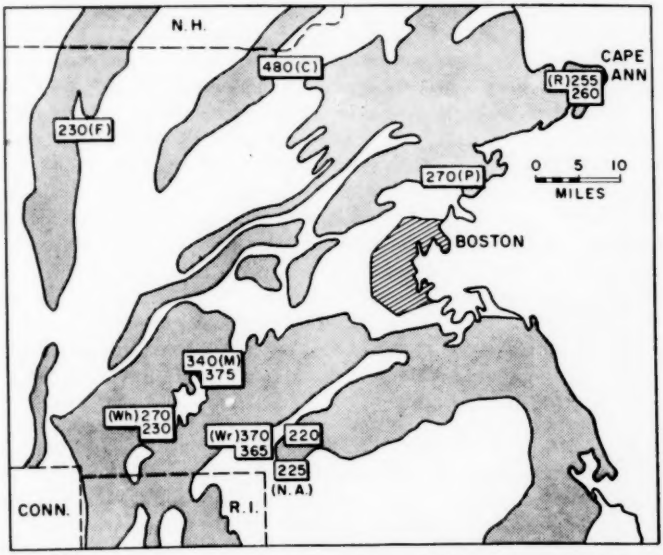


Fig. 2. Sketch map of granite areas of eastern Massachusetts, showing localities from which zircon was obtained and the corresponding age ratios (in millions of years). C—West Chelmsford, F—Fitchburg, M—Milford, N.A.—North Attleboro, P—Peabody, R—Rockport, Wh—Whitinsville, Wr—Wrentham.

that some of the rocks mapped as Dedham granodiorite are of an earlier period of intrusion.

These two ages, 260 MY and 355 MY, are fairly close to the rather common ages that have been appearing in the literature for many years for granitic rocks of the Appalachian province. The Quincy granite group of rocks (Peabody, Cape Ann, etc.) appears to be an extension of an alkaline belt of intrusives that includes the White Mountain magma series of New Hampshire and a number of alkaline masses extending northward into Canada. Whatever the actual geological age of these rocks might be, it appears that in time of implacement they form a homogeneous group with a number of other types of plutonic rocks appearing rather prominently in the northern part of the Appalachian province.

The discrepant age ratio found in the zircon from the Northbridge granite gneiss near Uxbridge (Whitinsville locality) appears to be more than simply precision error in analysis. It may be that these gneissic rocks were partly recrystallized during the time of emplacement of the granites to the northeast and east, with the zircon lowest in radioactivity (and therefore in damage resulting from radioactivity) having suffered the least recrystallization. This suggests that either the gneiss might have been Precambrian to start with, or the zircon may have been in part relict from Precambrian sediments.

The age ratio for zircon from the Fletcher quarry (West Chelmsford) likewise does not fit the pattern shown by the other localities. In this case, however, opinion regarding the history of parent granite is mixed, to say the least, some writers such as Currier and Jahns (1952) ascribing its origin to metasomatism. From this standpoint the age ratio of 480 MY could be interpreted as derived from zircon of mixed origin, in part from old (Precambrian ?) rocks, in part from much more recently crystallized granite of the 240 or 355 MY groups. Although relatively little zircon could be collected from this granite, there is evidence of slight rounding in some grains and of a crystal habit somewhat different from other granite zircons in eastern Massachusetts. More age determinations, from critical localities, are needed for the granites in the Chelmsford area.

The present results neither confirm nor negate the proposed Precambrian age for the granite at Hoppin Hill (Dowse, 1950). A granite sample collected within a few hundred yards of the critical outcrop yielded too little zircon for Pb analysis; the nearest locality for which an age ratio has been determined (225 MY) is three miles distant.

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Department of Geology and Geophysics
Massachusetts Institute of Technology
Cambridge, Massachusetts

# REVIEWS

*Science and the Human Imagination*; by MARY B. HESSE. P. 171. New York, 1955 (Philosophical Library, $3.75).—Scientists who are concerned with the broader implications of their work and who are interested in the relation of science to other areas of knowledge will welcome this book. It gives a bird's-eye view of the development of philosophy of science that will prove very useful to persons not expert in this area. It seems well suited for assisting students of science to gain a deeper understanding of science itself, and the first chapters especially will be valuable for use in those science courses designed for the non-science student.

The first part of the book is historical, describing the heredity of modern science and the environment of the Scientific Revolution, and giving a brief account of the subsequent development of science up to the 19th century.

The second part of the book is critical rather than historical, assessing the developments in philosophy brought on by modern physics. This is followed by an answer to the question of the significance of scientific theories in terms of an "essential realism which leaves room for interaction between science and its cultural environment," proposing that scientific theories describe nature analogically, not literally, yet not "entirely unrelated to the reality of nature."

Dr. Hesse has written this book in the hope that it may "contribute to a lessening of the tension between science and religion" by increasing the understanding of science. The reviewer is sympathetic to this objective, but even if the reader is not the value of the book remains since it is "for the most part a straightforward account of recent developments in the history and philosophy of science."

In contrast to many expositions of the development of modern science, this book points out the debt which the scientific revolution of the 16th and 17th centuries owes to the Christian tradition of the West.

ADRIAN DOCKEN

*Les Lacunes des Cristaux et leurs Inclusions Fluides;* by G. DEICHA. P. 126; 13 figs., 12 pls. (21 photomicrographs). Paris, 1955 (Masson et Cie., 950 francs).—This little book summarizes recent thinking about crystal cavities and the fluid inclusions they contain. Its contents are: Chapter 1, Growth-cavities and crystal structure; 2, Formation of bubbles by contraction of liquid in completely filled cavities; 3, Geologic thermometry and gas under pressure in minerals; 4, Proofs of deep origin of hydrothermal and pneumatolytic solutions; 5, Glassy inclusions and cavities containing solid deposits; Conclusion; General bibliography; Alphabetical index; List of illustrations; Table of contents. The book should become widely known for its new contributions as well as its brief but effective summary of the literature of fluid inclusions.

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